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PORCELAIN ENAMELING QUALITY STEEL

PLATES AND WELDMENTS

By

J. D. WALTON

and

J. N. HARRIS

Project Report 1

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Final Report

PROJECT NO. A-308

Atlanta
Engineering Experiment Station
Georgia Institute of Technology
1956 - 1958

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A-308

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

PROJECT REPORT NO. 1

PROJECT NO. A-308

HYDROGEN EXTRACTION APPARATUS

CONSTRUCTION AND OPERATION

DJ

By

J. D. WALTON

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CONTRACT NO. NObs 772209
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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

DECEMBER, 1956

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

PROJECT REPORT NO. 1

PROJECT NO. A-308

HYDROGEN EXTRACTION APPARATUS
CONSTRUCTION AND OPERATION

By

J. D. WALTON

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

DECEMBER, 1956

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LIST OF FIGURES

I. CONSTRUCTION OF APPARATUS

The apparatus shown in Figure 1 is that used for extracting hydrogen from steel, and consists of three basic components: gas burette, extraction chamber and base plate.

A. Construction of Gas Burette

The gas burette was made from two commercially available parts (Figure 2). The basic burette was obtained from the Scientific Glass Apparatus Company and is No. J1906, graduated in 0.05 ml divisions from 0-4 ml, in 0.2 ml from 4-15 ml and in 1.0 ml from 15-30 ml. The base of this burette is furnished with a small glass tube which was removed for our use and a 14/35 standard tapered female joint† was welded in its place.

B. Construction of Extraction Chamber

In Figure 3 the glass components of the upper portion of the extraction chamber are shown. The upper portion of the extraction chamber is composed of two items, a 6-inch length of 1-inch diameter Pyrex "Double-Tough" pipe and a 14/35 standard tapered male joint (Corning No. 6540). The 6 inch length of pipe was divided into two 3-inch lengths, each with one flared end. The unflared end was flame worked until it was reduced to the diameter of the straight end of the standard tapered male joint. This joint was then welded to the previously described 3-inch section of pipe, forming a section with a standard tapered 14/35 male joint on one end and a flared end of a standard 1-inch Pyrex pipe on the other. The lower portion of the chamber is composed of a Pyrex "Double-Tough" 2- by 1-inch pipe reducer†† (Figure 4).

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†Will Corporation, No. J1906 (Corning No. 6540).

††Corning Glass Works.

All of the components necessary to assemble the extraction chamber are shown in Figure 4. The flanges used to join the two glass components are standard flanges with molded inserts used to join sections of 1-inch diameter Pyrex "Double-Tough" pipe. The gasket between the pipe sections is a Teflon type-T gasket, also a stock item for 1-inch diameter pipe.

C. Construction of Base Plate

The base plate to which the extraction chamber was sealed is shown in Figure 5. The plate was constructed from one piece of 4- x 4- 1/4-inch stainless steel plate. Three holes were drilled, forming an equilateral triangle with sides of 3-3/8 inches, measuring from the center of each hole. The center of the index hole was located midway along one side of the plate 5/16 inch from the edge. The other two holes were located the same distance from the edge of their respective sides. These holes were tapped to receive 1/4-inch - 20 x 1-1/2-inch threaded studs. Three of these studs were screwed into the base plate flush with the back of the plate and silver-soldered in this position.

On a chord of the circle described by the studs, two 1/8-inch diameter holes were drilled 1/4 inch from the center of the circle and 5/8 inch from the point where a line through the center of the circle perpendicularly bisected the chord. On another chord, parallel with the first, a 1/16-inch diameter hole was drilled 1/4 inch on the opposite side of the center of the circle. The center of the circle was located at the point of intersect of the perpendicular bisect of a line through the center of the circle and the chord Into these holes stainless steel rods the same size as the holes were inserted flush with the bottom of the base plate and extending up through the top of the plate 1-1/4 inches. These stainless steel rods were silver-soldered to the bottom of the base plate.

The extraction chamber was secured to the base plate by means of a flange and molded insert designed for fastening 2-inch diameter Pyrex pipe sections. In this instance, the studs in the base plate extended through the flange, and 1/4-inch nuts were used to tighten the chamber against the plate. A Teflon type-T gasket available for 2-inch diameter Pyrex pipe was used to effect a seal between the extraction chamber and base plate.

D. Assembly of Three Main Components

Figure 6 shows the complete assembly of the apparatus.

II. ACCESSORY EQUIPMENT

Figure 7 shows the accessory equipment used in filling the apparatus. The 250-ml Erlenmeyer flask (Corning No. 5000) was used to hold the mercury for each extraction setup when the apparatus was not in use. The small long-stem funnel (Corning No. 6160) was used to fill the extraction setup with mercury and the 250-ml separatory funnel (Corning No. 6400) was used to separate the mercury from the butylphthalate after an extraction was made. The large short-stem funnel was used to filter the butylphthalate after each run to be sure that it remained clean.

TABLE I

REQUIRED MATERIAL

Quantity	Description	Vendor
1	Gas burette, No. J1906 graduated in 0.05 ml divisions from 0-4 ml, in 0.2 ml from 4-15 ml, and in 1.0 ml from 15-30 ml	A
1	Ground glass joints. Standard taper Pyrex glass No. 15821 (Corning No. 6540)	B

(Continued)

TABLE I (Continued)

REQUIRED MATERIAL

Quantity	Description	Vendor
1	3-foot length Polyethylene tubing, 1/4-inch inside diameter, 1/16-inch wall thickness	B
1	250-ml Erlenmeyer flask Pyrex glass with 24/40 standard taper joint and stopper No. 13686 (Corning No. 5000)	B
1	250-ml pear-shaped separatory funnel Pyrex glass. Standard taper stopper No. 16, stopcocks No. 2. No. 14376 (Corning No. 6400)	B
1	Funnel, long stem exact 60° Pyrex glass 65-mm diameter, 150-mm stem length. No. 14171 (Corning No. 6160)	
1	Funnel, short stem 125-mm diameter, 125-mm stem length No. 14146	B
6 feet	Extra heavy wall, rubber tubing, 1/4-inch inside diameter, 3/16-inch wall thickness No. 23496	B
1	Leveling bulb, Kimbel "K" brand 250 ml with vertical side tube connected at top and bottom	C
1	Pyrex "Double-Tough" pipe reducer, 2-inch x 6-inch length Pyrex "Double-Tough" pipe, 1-inch diameter	D
2	Molded inserts for 1-inch pipe	D
1	Molded insert for 2-inch pipe	D
2	Standard flanges for 1-inch pipe	D
1	Standard flanges for 2-inch pipe	D
1	Teflon type-T gasket for 1-inch pipe	D
1	Teflon type-T gasket for 2-inch pipe	D
3	5/16-inch, 18- x 1-1/2-inch bolts	D
3	5/16-inch, 18-nuts	D

(Continued)

TABLE I (Concluded)

REQUIRED MATERIAL

Quantity	Description	Vendor
1	4 x 4 x 1/4-inch stainless steel plate	
3	1/4-inch-20 x 1-1/2-inch stainless steel studs	
3	1/4-inch-20 stainless steel nuts for studs	
1	450-watt, 115-volt hot plate, No. 61725	E
1	Cenco Hyvac Pump	F

TABLE II

MANUFACTURERS OF REQUIRED MATERIALS

Vendors	
A	Scientific Glass Apparatus Co. 105 Lakewood Terrace Bloomfield, New Jersey
B	Will Corporation New York 12, New York (Catalog 6)
C	Arthur H. Thomas Co. Philadelphia, Pennsylvania (1950 Catalog)
D	Corning Glass Works Corning New York
E	Precision Scientific Co. Chicago, Illinois
F	Central Scientific Co. Chicago, Illinois

III. OPERATION

A. Uncoated Metal

If the metal to be studied is uncoated, no pretreatment of the specimen is required unless heavy scale is to be removed. This may be done by light sandblasting--only enough blasting to remove lightly adhering scale.

A 2- x 1-1/2-inch specimen is used in this apparatus. The specimen is placed on the base plate, with one side against the 1/16-inch rod, and the other side against the two 1/8-inch rods. The 2-inch dimension of the specimen is perpendicular to the base plate.

The Teflon gasket is then placed on the bottom of the extraction chamber and the chamber is placed over the specimen and secured in this position by means of the 1/4-inch-20 nuts. The seal should be sufficient at this point to keep the mercury from leaking when put into the extraction chamber.

Mercury is poured into the extraction chamber until the level of the mercury reaches the necked-down portion of the 2- x 1-inch Pyrex pipe reducer.

One end of the 6-foot length of heavy wall rubber tubing is then slipped over the 14/35 standard taper joint on the top of the extraction chamber. The other end of this tubing is connected to a vacuum pump. A vacuum of 3 mm of mercury is applied to the system to remove all entrapped gases. The 1/4-inch-20 nuts are tightened sufficiently to reduce leakage to no more than one bubble every 5-10 seconds. The vacuum is then removed and the remainder of the chamber filled with butylphthalate.

The gas burette is placed on the extraction chamber and approximately 150 ml of butylphthalate is poured into the leveling bulb with the height of the bulb kept below the top of the extraction chamber.

With the stopcock on the top of the gas burette open, the leveling bulb is raised until the level of the butylphthalate reaches the top of the glass tube within the lower portion of the gas burette. This level is increased until the butylphthalate runs down the tube and fills the volume between the top of the extraction chamber and the lower portion of the gas burette. If the butylphthalate level were raised before the volume were filled, it would bridge over the top of the small tube, trapping air in this space. Once this volume is filled, the leveling bulb is raised until the entire gas burette is filled and butylthalate rises into the neck above the stopcock. The stopcock is then closed. The leveling bulb is then hung in a convenient location and the apparatus is placed on a hot plate.

The hot plate is adjusted to provide a constant mercury temperature of 175° C. Heating is continued until all gases have been expelled from the metal. No gases are assumed to remain when no bubbles are seen over a period of 30 minutes.

When recording the volume of gas liberated, it is advisable to tilt the apparatus carefully, first to one side and then to the other, to insure the liberation of any bubbles which might be trapped under the metal or between the metal and the walls of the extraction chamber.

After the extraction operation has been completed, the apparatus is allowed to cool. The leveling bulb is lowered to a position below the extraction chamber, and the stopcock on the gas burette is opened. All the butylphthalate is thus drained from the gas burette and the burette is removed.

The liquid contents of the extraction chamber are poured into a separatory funnel and the apparatus is dismantled. The mercury is drained from the separatory funnel into a glass stoppered Erlenmeyer flask. The butylphthalate is then drained through a funnel and filtered into another flask for storage.

B. Coated Metal

When a ceramic-coated metal is to be studied with respect to the hydrogen injected into it through the enameling operation, the following procedure is followed:

The metal is prepared for coating by sandblasting. The coating is applied by spraying or dipping and fired under the specified conditions. When the specimen is removed from the furnace it is immediately plunged into ice water. As soon as the specimen is cool it is again sandblasted to remove all traces of coating and is immediately set up in the extraction apparatus as previously described.

Respectfully submitted:

J. D. Walton
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

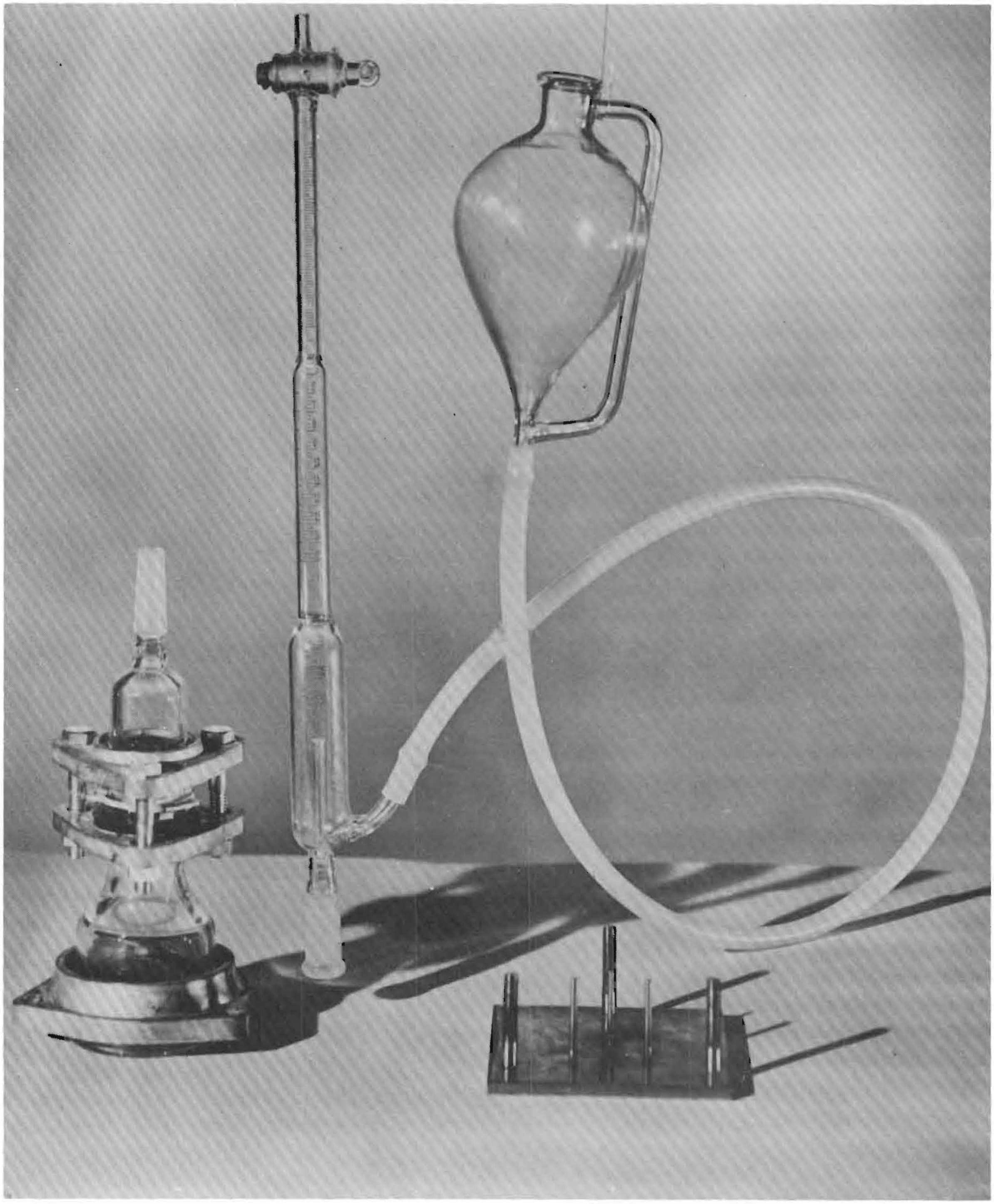

Figure 1. Basic Components of Extraction Apparatus.

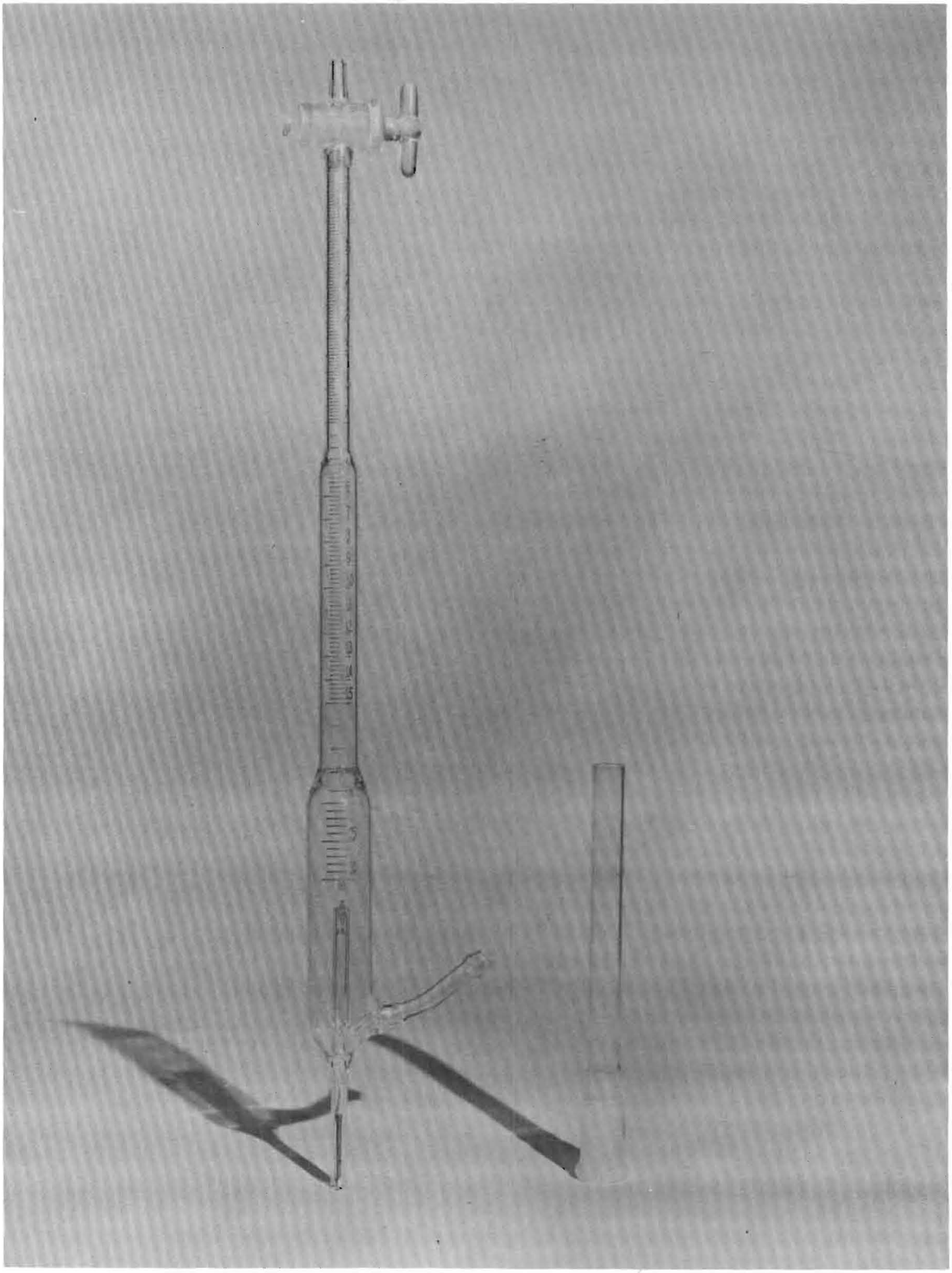

Figure 2. Basic Components for Construction of Gas Burette.

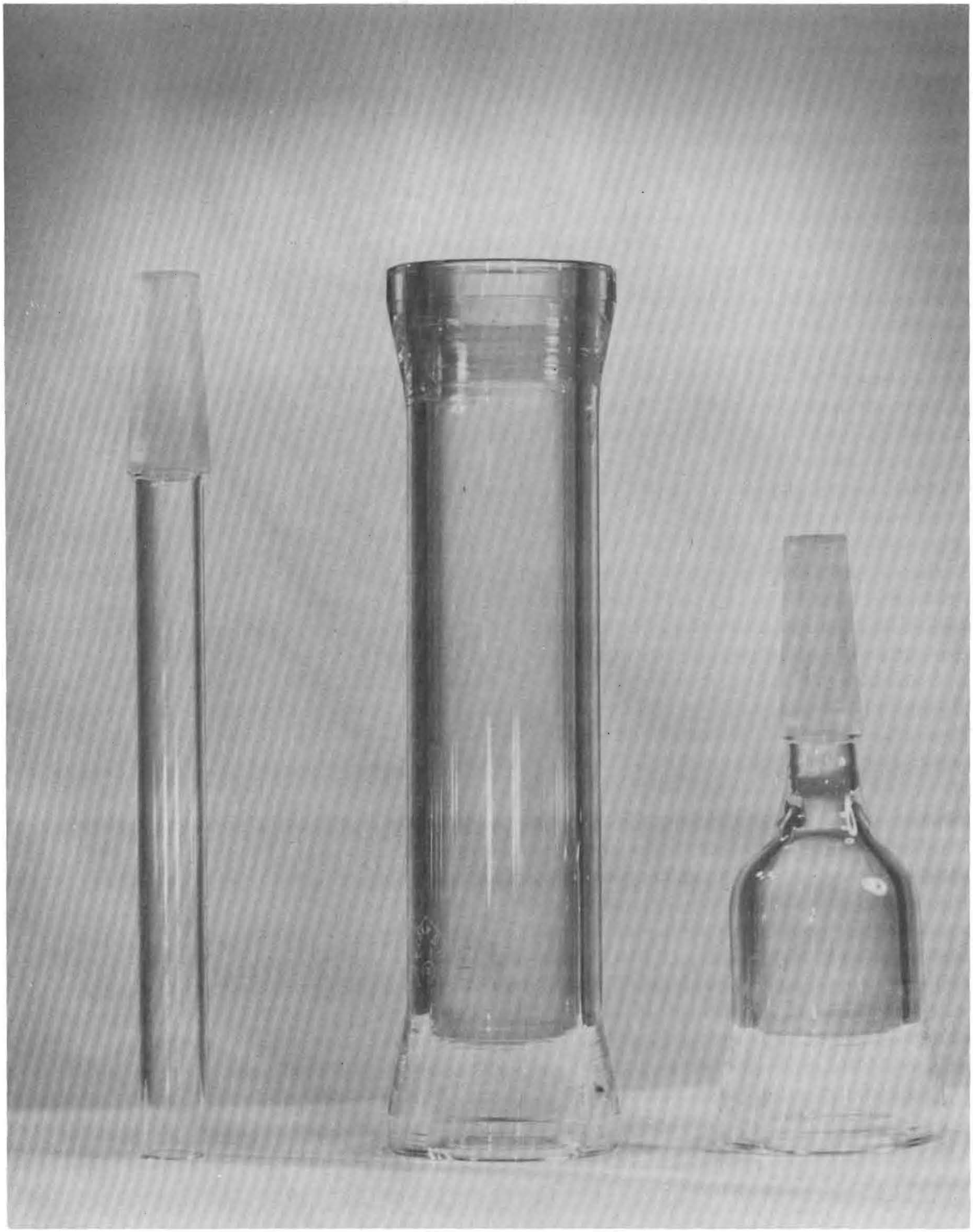

Figure 3. Basic Components of Construction for Upper Portion of Extraction Chamber.

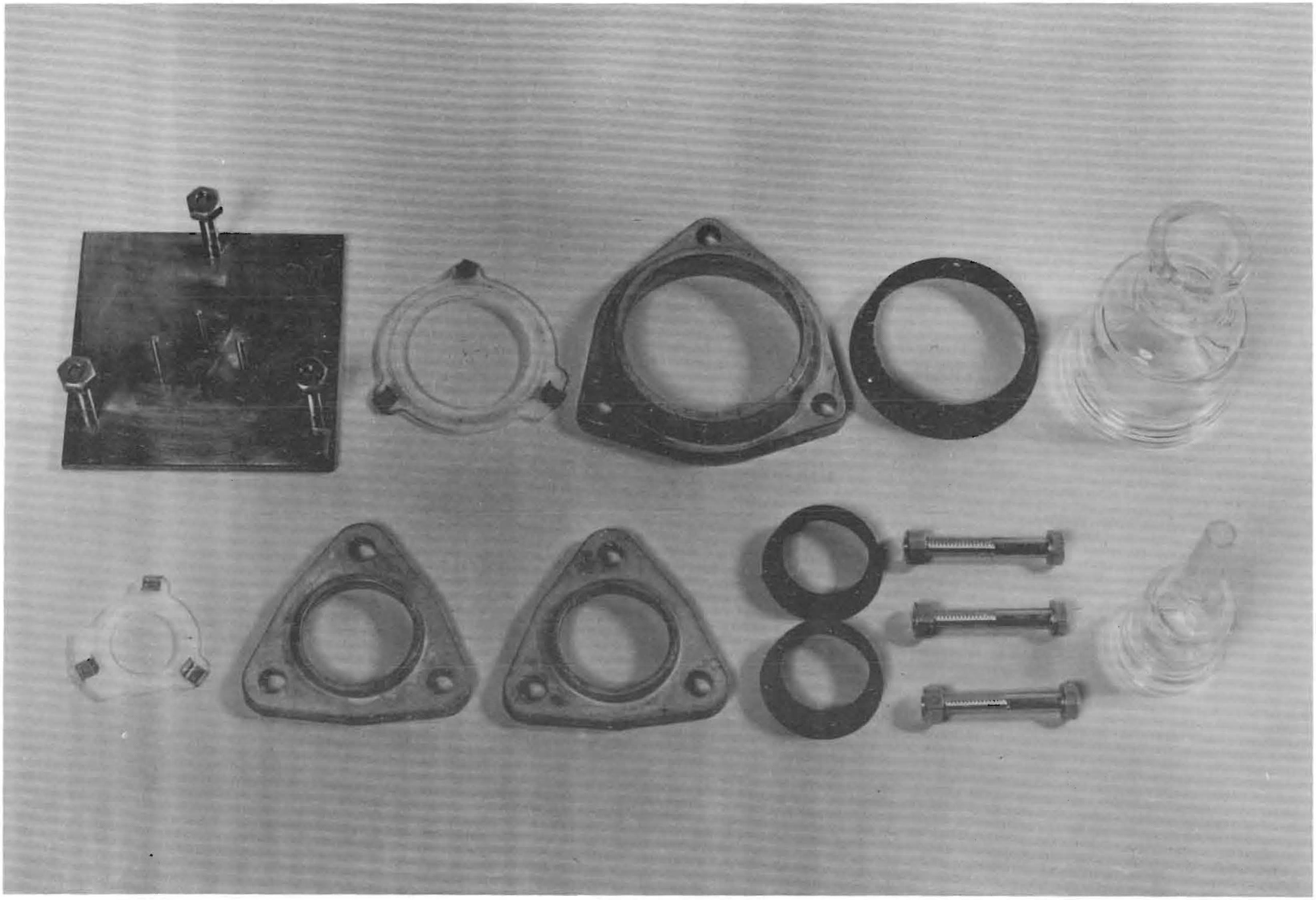

Figure 4. All Components of Extraction Chamber.

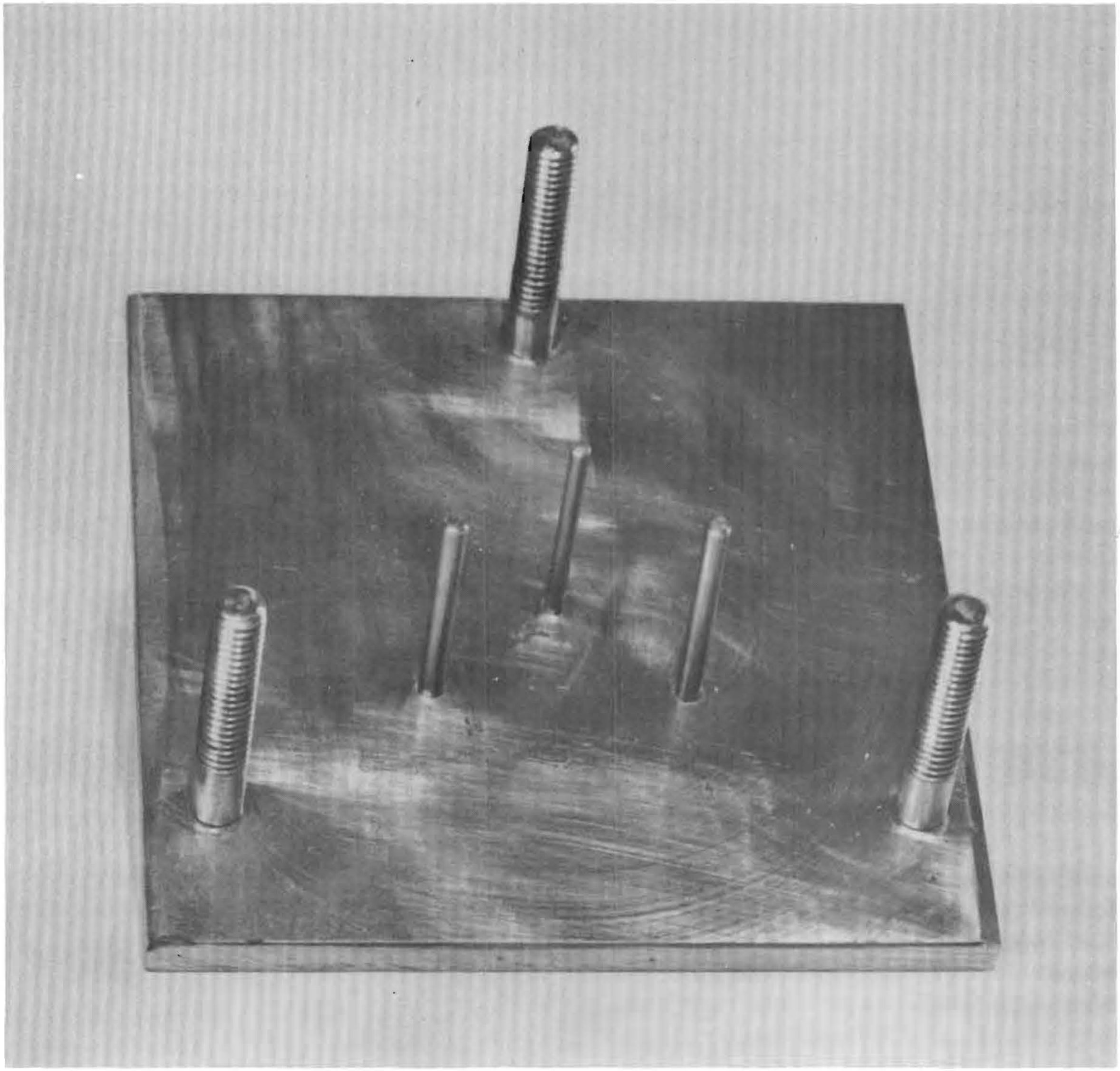

Figure 5. Base Plate.

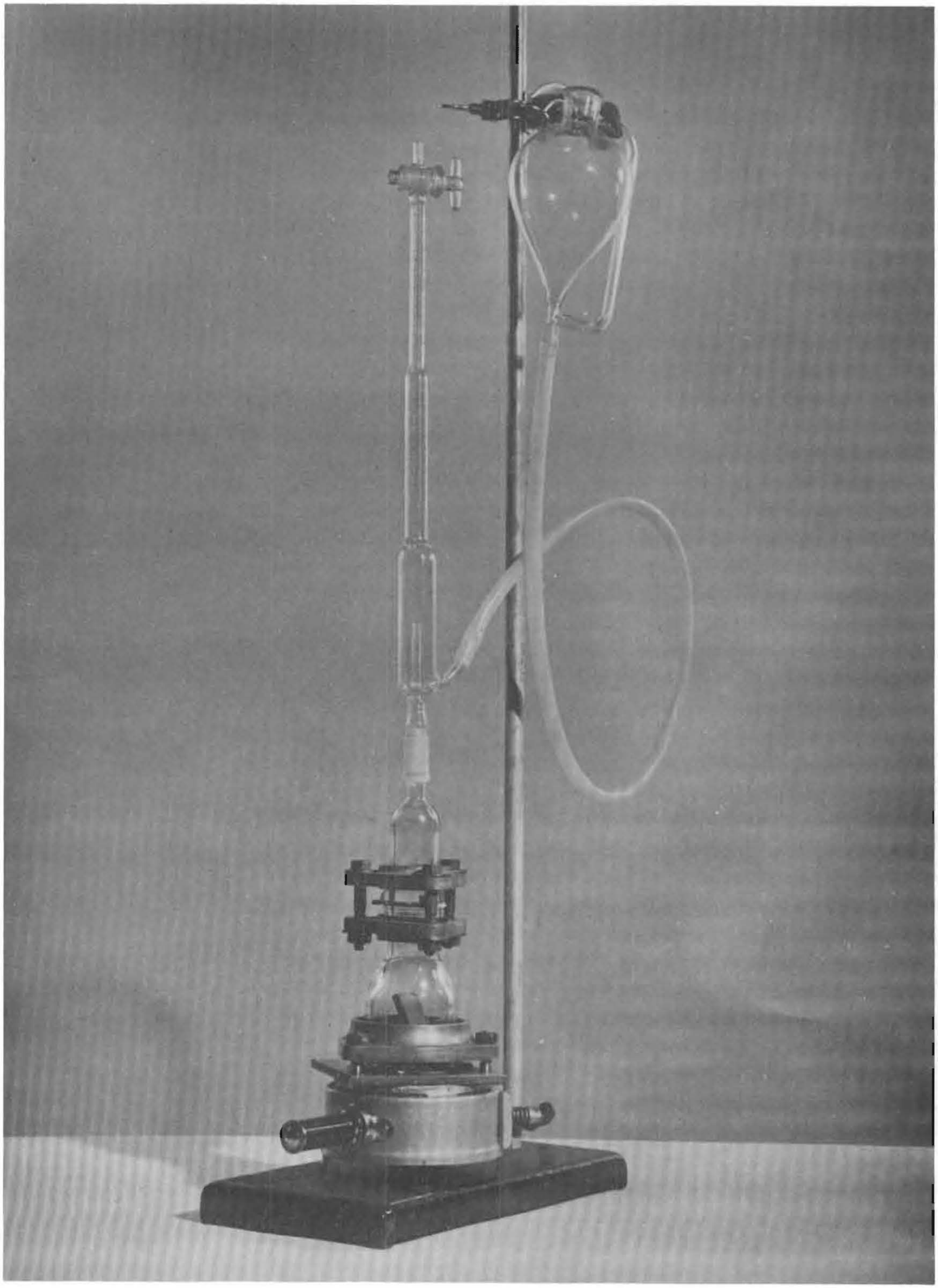

Figure 6. Assembly of All Parts of Extraction Apparatus.

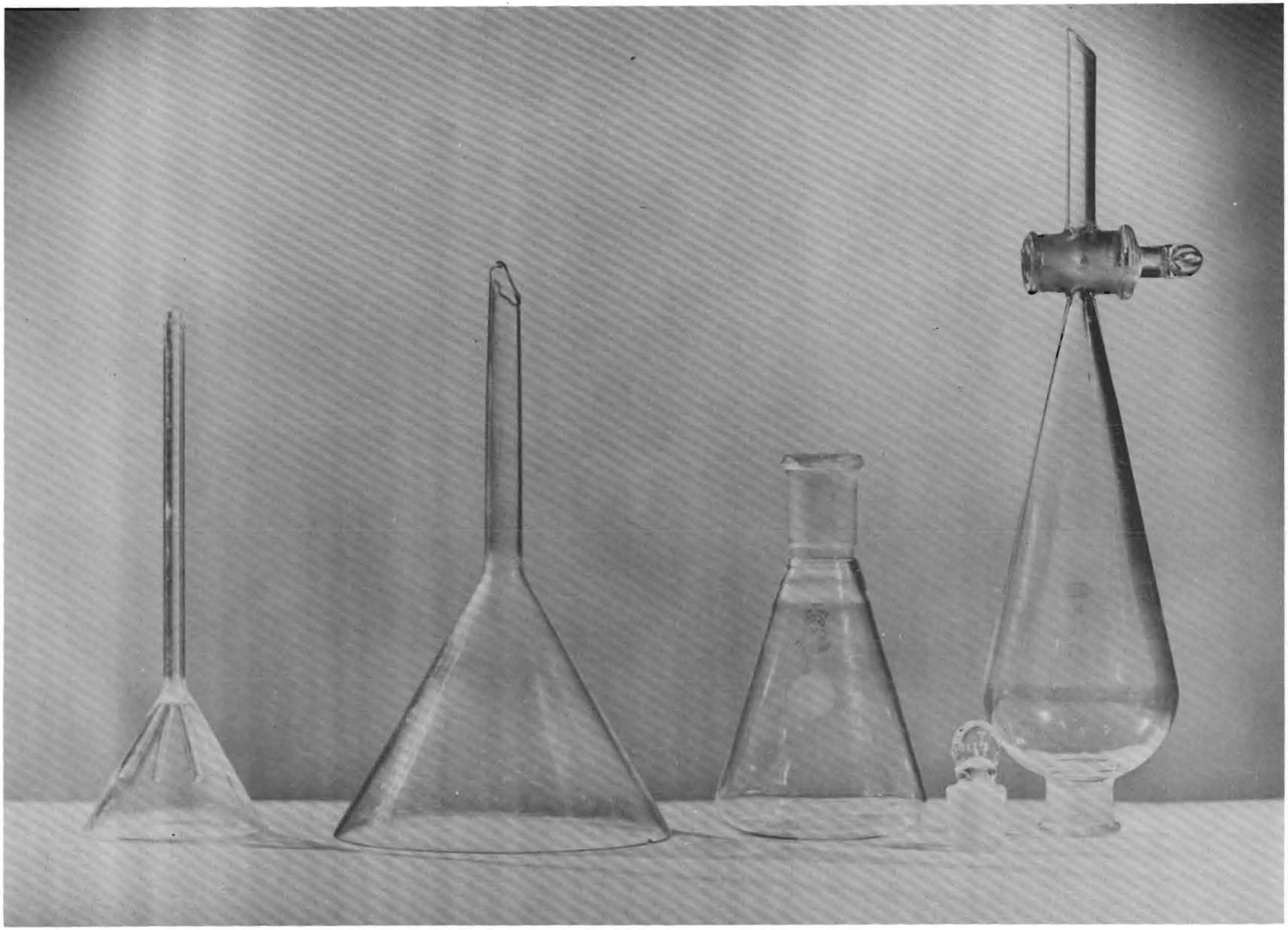

Figure 7. Accessory Equipment.

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STATUS REPORT NO. 1

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By

J. D. Walton and J. N. Harris

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

JANUARY 1, 1957

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

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By

J. D. Walton and J. N. Harris

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

JANUARY 1, 1957

Status Report No. 1, Project No. A-308

I. SUMMARY

Porcelain enamel frits were secured from four different manufacturers, and applied to steel which readily produced fish scales when enameled in a moist atmosphere. These enamels were milled with 0 and 20 percent alumina, fired on 4-by-8-by-3/16-inch plate and thermal shocked.

Sufficient quantities of steel plate for fabricating T-joint specimens and frits have been ordered to provide an adequate supply of the basic materials for study.

Additional units of hydrogen extraction apparatus have been fabricated to bring the total on hand to five.

II. EXPERIMENTAL PROGRESS

A. Preliminary Frit Evaluation

Low temperature porcelain enamel frits were secured from the following manufacturers: Chicago Vitreous Corp., Ferro Corp., the O. Hommel Co., and Pemco Corp.

Since alumina additions to enamels improve their thermal shock resistance, but require higher firing temperatures, it was decided that these newly developed low-temperature ground coat frits would be used in this phase of the project. Thus, maximum aluminum oxide could be added before firing temperatures generally used in industry would be exceeded.

The following mill addition was selected:

100	Frit
6	O'Hommel Clay 540
4	SiO_2
1/2	Borax
1/8	Bentonite
1/8	$MgCO_3$
50	Water

All frits were milled with this mill addition and fired at 1350°F in dry and wet atmospheres on 3/16-inch steel plate which produced fish-scale when enameled in a moist atmosphere with the "conventional" enamels used under Contract NObs-66521. In no instance were any fish scale produced even when the moisture content of the furnace atmosphere was raised to 100 ml of H_2O per cubic foot of furnace volume.

In order to confirm the fish-scale producing property of this steel, it was coated with the enamel used under Contract NObs-66521 in a normal and wet (100 ml/cu. ft) atmosphere. Both conditions produced fish-scale. In the latter case, the surface of the enameled plate was literally covered with fish-scale. The greatest distance between any two fish scales was no greater than 1/8-inch.

Each of the enamels was next milled with 20 percent calcined unground alumina (Alcoa A-1). A 4-by-8-by-3/16-inch plates of the same steel used above was coated with each enamel with and without the alumina. The firing schedule of the alumina free enamel was 1325°F for 17 minutes and 1400°F for 17 minutes for the enamels with 20 percent alumina. All plates were subjected to the thermal shock schedule of MIL-P-16961B including the 5 quenches from 900°F.

The plates coated with the enamels containing 20 percent alumina showed no effect from the thermal shock treatment, even on the edges of the plate. These enamels had a very satin finish due to the alumina addition and kept this finish throughout the thermal shock treatment. The plates coated with the alumina free enamel passed the thermal shock test, however, the surface which was very smooth and glassy prior to shocking was sandy to the touch and had a "frosty" appearance after the thermal shock treatment.

All of these frits were secured in sufficient quantities to insure a constant frit composition for the mill addition, steel composition and welding electrode studies.

B. Hydrogen Extraction Apparatus

Project Report No. 1 was written describing the construction and use of the hydrogen extraction apparatus. Two additional hydrogen extraction units were constructed in order that five samples may be run simultaneously.

C. Steel Procurement

Sufficient quantities of AlSl C1010 steel plate, 3/16-inch and 58/8-inch thick were ordered from which all the T-joint specimens will be made for use in the frit, mill addition and welding electrode evaluation studies.

III. FUTURE WORK

T-joint specimens which have been fabricated will be coated with each of the frits containing 0, 10, 20, and 30 percent aluminum oxide and thermal shocked according to the schedule of MIL-P-16961B.

Hydrogen extraction data will be obtained for each frit under high and low humidity conditions with each of the alumina contents listed above.

Tearing and fit characteristics of each enamel will also be determined.

Alumina in a vitreous form rather than calcined will be substituted for the A-1 alumina in order to evaluate the thermal shock resistant properties imparted by this type of alumina.

Respectfully submitted,

J. D. Walton
Project Director

J. N. Harris
Research Assistant

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 2

PROJECT NO. A-308

By

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

MARCH 1, 1957

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 2

PROJECT NO. A-308

By

J. D. Walton and J. N. Harris

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

MARCH 1, 1957

Status Report No. 2, Project No. A-308

I. SUMMARY

Techniques of dipping enamels with high alumina content were developed, but problems encountered in draining and firing were severe enough to require reevaluation of the advantages of high Al_2O_3 content.

Hydrogen extraction work was begun with the hydrogen determined as a function of firing temperature and Al_2O_3 content.

Oxidation studies were begun with the amount of oxidation as a function of carbon content and firing atmosphere.

Wettability studies were made with the enamel spread as a function of carbon content and firing atmosphere.

The steel to be used throughout the enamel evaluation studies was received.

II. EXPERIMENTAL PROGRESS

A. Dipping of T-Sections

Techniques were developed for dipping T-sections in enamels containing as much as 20 per cent of calcined alumina so that only a few drain lines were visible on dried T-sections.

Enamels containing 20 per cent alumina were prepared for dipping from each of the frits obtained from Pemco Corporation, Chicago Vitreous Corporation, the O'Hommel Company and the Ferro Corporation. The following mill addition was used for all enamels.

100	Frit
6	O'Hommel Clay 540
4	SiO_2
20	Alcoa A-1 Alumina (unground)
1/2	Borax
1/8	Bentonite
1/8	$MgCo_3$
65	Water

T-sections were dipped with each of these enamels and fired at 1400°F for 25 minutes. Tearing and hair lines which developed on heating did not heal over during the latter portion of the firing cycle. There was no evidence that the tearing or hairlines tended to heal even when the firing temperature was raised to 1500°F. Three-sixteenths plate, coated by dipping with enamels containing 10 per cent calcined alumina, gave smoother surfaces with no tearing. Further work in dipping T-sections will be directed toward using enamels containing less than 20 per cent calcined alumina.

B. Hydrogen Extraction

In an effort to obtain a quenching medium which would not react with steel at 1400°F when plunged into it, carbon tetrachloride was selected. Two samples of 1012 steel cut from the same stock were enameled and fired in an atmosphere of dry air for 22 minutes at 1400°F. One sample was quenched in carbon tetrachloride and the second sample was allowed to cool slowly in the air. The sample quenched in CCl_4 gave 0.41 mls. of gas and the air-cooled sample gave only 0.05 mls. of gas. Since quenching is used to cool rapidly an enameled specimen to entrap the hydrogen, and the coating remains essentially intact, it was decided that water would continue to be used as the quenching medium.

Work on hydrogen extraction as a function of Al_2O_3 content has been started. All firing has been done at 1400°F in an atmosphere provided by passing dry air through water at 25°C. All samples have been cut from the same stock of C1012 Atlantic steel. Enamels prepared from Pemco Corporation frits gave an increasing amount of gas as Al_2O_3 content was increased. Enamels prepared with frits from Chicago Vitreous Corporation and Ferro Corporation gave decreasing amounts of gas as Al_2O_3 content was increased.

C. Oxidation Studies

Five steels with carbon contents of 0.04, 0.10, 0.19, 0.27 and 0.36 percent, respectively, were selected for oxidation studies. These steels were fired in atmospheres of dry air, wet air and CO_2. Samples were weighed before and after firing to determine weight of oxide gained. All firing was at 1400°F. The steels fired in atmospheres of wet and dry air gave decreasing amounts of oxide as the carbon content of the steels increased. The steels fired in an atmosphere of CO_2 increased in weight as the carbon content of the steel increased. In all cases reproducibility of results was better with the high carbon steels.

D. Wettability Studies

Wettability studies were conducted in the following manner. Enamels were prepared from each of the manufacturers' frits. These were dried and pressed into pellets. The pellet was placed on a section of metal and the spread of the pellet upon firing was measured.

Enamels were prepared, containing 0, 10, and 20 per cent Al_2O_3. Pellets made from enamels containing 20 per cent alumina would not fuse down even at very high temperatures. Pellets made from enamels containing 0 and 10 per cent alumina were placed on steels with carbon contents of 0.04, 0.10, 0.19, 0.27 and 0.36 per cent respectively. These tests were conducted in both wet and dry atmospheres. Very little difference in the spread of the pellets was noted with varying carbon content of the steel.

III. FUTURE WORK

New T-joint specimens will be fabricated with the AISI C1012 steel received. Further studies in dipping of T-joints will be made with enamels containing less than 20 per cent alumina. Thermal shock tests will be conducted according to the schedule of MIL-P-16961B.

Hydrogen extraction tests will be continued in wet and dry atmospheres using enamels on steels of various carbon contents.

Oxidation studies will be continued on each steel.

Wettability studies will be continued on each enamel and each steel.

Respectfully submitted,

J. D. Walton
Project Director

J. N. Harris
Research Assistant

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

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ENGINEERING EXPERIMENT STATION
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Atlanta, Georgia

STATUS REPORT NO. 3
PROJECT NO. A-308

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON and J. N. HARRIS

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JULY 1, 1957

ENGINEERING EXPERIMENT STATION
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STATUS REPORT NO. 3
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PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

JULY 1, 1957

I. SUMMARY

Hydrogen extraction tests were completed on steels having a carbon content range of 0.04 to 0.44 per cent. These tests were run with the enamels received from the following manufacturers: The Pemco Corporation, Chicago Vitreous Corporation, Ferro Corporation, and the O. Hommel Company.

Attempts to control bubble film in an effort to reduce fishscaling tendencies were made by changing various mill additions in the four basic enamel compositions received from the manufacturers listed above.

A study of tendency to fishscale with increase in carbon content of steel was made. Fishscaling increased as carbon content increased.

A supply of fused alumina was received (Alundum 38x, The Norton Company) and is being used in evaluating its properties as compared with calcined alumina.

Adherence tests were run to evaluate the effects of calcined and fused alumina mill additions on enamels.

Tearing tests were started to evaluate the effect of calcined alumina, fused alumina and silica mill additions on enamels.

Welding studies were started. Some welds fishscaled and some did not, even though the same enamel was applied to the welds and all were fired under the same conditions.

II. EXPERIMENTAL PROGRESS

A. Hydrogen Extraction

Hydrogen extraction studies were completed on steels with carbon contents of 0.04, 0.12, 0.19, 0.27 and 0.44 per cent. Tests were run with the enamels received from Pemco Corporation, Chicago Vitreous Corporation, Ferro Corporation and the O. Hommel Company. Tests were also run with each of the above four enamels containing 10-per-cent additions of calcined alumina. A decrease in the amount of gas extracted was noted for all enamels with the 10-per-cent addition of alumina. No definite relationship was noted between gas extracted and carbon content of steel.

B. Mill Addition Studies

As noted in Summary Report No. 1, the size of the bubbles in the bubble film seems to control fishscaling. Three enamels were made with O. Hommel frits substituting Ferro's Green Label Clay, Red Label Clay and Black Label Clay, for the O. Hommel No. 540 clay. These enamels were sprayed on 3/16-inch C1012 steel plates and fired in a wet atmosphere. The plate coated with the enamel made with Ferro's Green Label Clay had large, well spaced bubbles in the bubble film and had very few fishscale. The enamel containing Red Label Clay had slightly smaller bubbles in the bubble film than the previous plate and had many more fishscale. The enamel made with Ferro's Black Label Clay had very small bubbles in the bubble film and fishscaled severely.

The following formulation was the standard formulation used in all mill addition studies:

100[†] frit

6 O. Hommel Clay #540

4 SiO_2

1/2 Borax

1/8 Bentonite

1/8 $MgCO_3$

50 Water

All studies used variations of this formula.

The clay content of an enamel was varied from one to nine parts clay. At from one to three parts clay the enamel fishscaled severely. The bubbles were only very slightly smaller than the bubbles obtained with six parts clay. At from four to six parts clay the enamel fishscaled about the same and the bubbles were the same. Fishscaling decreased above six parts clay. Bubble size also decreased and the clay began to have an effect similar to the effect of additions of alumina.

Work is now in progress on evaluation of additions of from 0 to 20 parts of silica. Less than four parts silica gave a very short firing range. Ten parts silica gave a much wider firing range and very little fishscale. Bubbles were large and well spaced. Mill additions of more than ten parts of silica will be studied in future work.

C. Fishscale Versus Carbon Content

Plates were cut from steels of carbon contents ranging from 0.05 to 0.44 per cent and enameled with two enamels, one which had very little tendency to

[†]Parts by weight.

fishscale on C1012 steel and the other which fishscaled severely on C1012 steel. Fishscaling increased as carbon content increased with either enamel, although no detectable difference could be seen in the bubble film from plate to plate as carbon content increased.

D. Adherence Tests

Adherence tests were run to compare the adherence of enamels containing fused and calcined alumina. In all cases the adherence of the enamels containing fused alumina was as good as the adherence of the enamels containing calcined alumina. The adherence of the enamels containing fused alumina developed at a lower temperature than those containing calcined alumina.

E. Tearing Tests

The four enamels received from the four manufacturers were evaluated for tearing and hairlining. Mill additions of fused and calcined alumina were also compared for hairlining and tearing. Tests were started with silica additions to the enamel. Tearing was very bad with 20-per-cent additions of calcined alumina. The best results were obtained with 20-per-cent additions of fused alumina.

Further work will utilize additions of fused alumina and silica.

F. Welding Studies

In order to study enamel defects in welds it was first necessary to produce welds that would fishscale. Two welding rods were secured which produced welds that fishscaled when coated with an enamel that was very susceptible to fishscaling. These are AWS E 10013 and AWS E 10016. Bubbles appeared the same on the C1012 steel as across the weld deposited by each of these rods.

AWS E 6013 and AWS E 6016 welds would not fishscale when coated with enamel even though the metal on each side of the weld fishscaled severely.

Samples are presently being mounted to determine if there is a difference in grain size of the weld metal for the different rods.

In an effort to stop fishscaling on the welds (by allowing gas to escape) 1/16-inch holes were drilled 3/4 of an inch apart across the center of the weld. This did not stop the fishscaling. Further work on welding studies will be directed toward preventing fishscaling on the welds.

III. FUTURE WORK

T-sections will be coated with enamels containing 10 and 20-per-cent fused alumina and evaluated for thermal shock resistance.

Tearing and fit characteristics will be determined for enamels containing higher percentages of silica.

Welding studies will be continued to determine the cause of fishscaling on welds.

Hydrogen extraction tests will be run on welds to determine if the amount of gas injected by various rods can be correlated with the tendency to fishscale.

Respectfully submitted:

J. D. Walton
Project Director

J. N. Harris
Research Assistant

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

C-1

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 4

PROJECT NO. A-308

PORCELAIN ENAMELING
QUALITY STEEL PLATE AND WELDMENTS

By

DJ

J. N. HARRIS AND J. D. WALTON

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CONTRACT NO. NObs 72209
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 312
DEPARTMENT OF THE NAVY

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

NOVEMBER 15, 1957

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 4

PROJECT NO. A-308

PORCELAIN ENAMELING QUALITY STEEL PLATE AND WELDMENTS

By

J. N. HARRIS AND J. D. WALTON

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

NOVEMBER 15, 1957

I. SUMMARY

Steels of four different compositions have been received from three different sources in sufficient quantity to assure a large number of tests in order to establish a specification for steel plate acceptably receptive to porcelain enamel coatings. A program has been set up for this phase of work as discussed with the Bureau representative and work is now underway.

II. EXPERIMENTAL PROGRESS

A paper given by J. H. Healy and J. D. Sullivan of the A. O. Smith Corporation at the May meeting of the American Ceramic Society described a process for treating steels by exposing the steels to cathodically generated hydrogen until a decrease in density and an increase in porosity is obtained. The change in structure may be noted by ultrasonic mechanical vibrations. After removal of a substantial portion of the hydrogen, glass may be applied to the steel and be free of high and low temperature hydrogen defects. This process allows the use of nonpremium steels, use of nonbubbly mill additions, and use of ground coat compositions which have greater corrosion resistance.

It is believed that voids in the steel can hold large amounts of hydrogen and cause, or not cause, delayed fishscaling defects according to the size and number of voids in the steel. The amount of hydrogen extracted from a steel when it is coated with a standard enamel and fired under standard conditions can be used as a measure of the ability of a steel to be successfully porcelain enameled. It appears that if an addition of alumina to a standard enamel causes a decrease in the amount of extractable gas from a steel over that extracted from the steel coated with the standard enamel not containing alumina then the tendency of the coated steel to fishscale is decreased. If the addition of alumina causes an increase in the amount of extractable gas the tendency of the coated steel to fishscale is increased. By measuring the amount of gas extracted from various steels when coated with a standard enamel and with this enamel containing mill additions of alumina a measure of the ability of a steel to be successfully enameled without defects can be obtained.

Steel has been obtained in sufficient quantity to run a large number of tests to validate previous testing.

Hot rolled steel plate in thicknesses of 1/4 and 3/16 inch in the following carbon content ranges (percentages) has been procured from Atlantic Steel Company and J. T. Ryerson and Son: (0.1-0.2), (0.3-0.4) and (0.4-0.5). In addition, cold finished 3/16-inch strip has been secured in a grade ranging in carbon content from 0.15 to 0.20 per cent.

Hydrogen extraction tests are being run on all steels. Sufficient samples are being run to insure reproducibility of results.

The following formulation is being used for all tests with additions of 5-, 10- and 15-per-cent fused alumina (Norton Alundum 38X).

	Parts by Weight
O. Hommel 230	65
O. Hommel 231	15
O. Hommel 232	20
O. Hommel Clay 540	6
Silica	4
Borax	1/2
Bentonite	1/8
Magnesium Carbonate	1/8
Water	50

The enamel is milled to a fineness of 6 to 8 gm retained on a 200-mesh screen (50-ml sample) after washing and drying. Specific gravity of the enamel is adjusted to 1.6 and samples are coated by dipping.

The following tests are being run concurrently with the hydrogen extraction tests. Larger samples of steel plate are being coated and fired under the same conditions as the hydrogen extraction samples. These samples are being set aside and observed for fishscale. One set of samples is being allowed to remain under room temperature conditions. The second set of samples is being heated to 175° C for 48 hours and the temperature raised 5 times in increments of 50° C after each 48-hour period.

Thermal shock tests are being carried out by the method described in Summary Report No. 2.

T-sections are being fabricated from each steel to be coated and fired.

III. FUTURE WORK

Work will continue on hydrogen extraction and other tests in an effort to set specifications for steel plate acceptably receptive to porcelain enamel coatings.

Respectfully submitted:

J. N. Harris
Project Director

Approved:

J. D. Walton, Head
Ceramic Branch

Wyatt C. Whitley, Chief
Chemical Sciences Division

c-1

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SUMMARY REPORT NO. 1

PROJECT NO. A-308

By

J. D. WALTON and J. N. HARRIS

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CONTRACT NO. NObs 72209
INDEX NO. NS-061-087
BUREAU OF SHIPS CODE 312
DEPARTMENT OF THE NAVY

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

MAY 1, 1957

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SUMMARY REPORT NO. 1

PROJECT NO. A-308

By

J. D. WALTON and J. N. HARRIS

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CONTRACT NO. NObs 72209
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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

MAY 1, 1957

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Summary Report No. 1, Project No. A-308

I. SUMMARY

Techniques of dipping T-sections with high alumina content enamels have been developed, but draining and firing problems have been severe enough to cause re-evaluation of the advantages of enamels containing high percentages of alumina.

Thermal shock tests have been conducted according to Mil-P-16961B with four low temperature ground coats containing a 10 percent mill addition of A-1 alumina. The ground coats were made from the frits received from the following manufacturers: the Ferro Corp., Chicago Vitreous Corp., the O'Hommel Co., and the Pemco Corp.

Hydrogen extraction studies have indicated that an increase in the percentage of alumina added as a mill addition to enamels causes a decrease in the amount of gas extracted.

Adherence as a function of content of alumina (Al_2O_3) has been established.

Oxidation and wettability studies have been completed on five steels ranging in carbon content from 0.04 to 0.36 percent.

II. INTRODUCTION

This project was initiated on October 31, 1956 and has as its objectives:

a. to develop a complete and technically accurate description of steel plates and welds of steel plates acceptably receptive to porcelain enamel coatings. This description will be incorporated into material specifications for Government procurement,

b. to determine the factors which affect the enameling characteristics of steel plates and welds,

c. to establish the validity of parameters and set limits for control of quality for enamelability of steel plates and welds, and

d. to assess the factors responsible for defective coated parts intended to conform to Specifications Mil-P-16961.

III. EXPERIMENTAL PROGRESS

A. Dipping Techniques

After studying various dipping techniques it was found that a T-section could be dipped and hung to dry with relatively few drain line markings. The manner in which the T-section is hung to dry is shown in Figure 1.

T-sections were prepared for dipping by sandblasting. The enamel was adjusted to a consistency somewhat thinner than that normally used for spraying. The T-section was then immersed in the enamel and rubbed thoroughly by hand. Hooks were passed through the holes as shown in Figure 1, and the T-section was lifted quickly straight up out of the enamel. The drainings that collected along the lower edge were removed with the fingertip. The T-sections were allowed to dry for 5 minutes in the air and then placed in a dryer at 110° C for completion of drying. The composition of all enamels used was as follows:

100	frit
6	O'Hommel clay #540
4	SiO_2
1/2	Borax
1/8	Bentonite
1/8	$MgCO_3$
55	Water

Fineness was 6 to 8 grams retained on a 200-mesh screen (50-cc sample). Specific gravity was 1.7. The percentage of Al_2O_3 was based on the frit and for every 10 percent increase of alumina 5 percent water was added.

The resultant coatings were very smooth on firing and exhibited very few drain line markings.

It was found that T-sections could be dipped in enamels containing up to 10 percent Al_2O_3, with the exception of the Pemco enamel. The Pemco enamel exhibited tearing and blistering with a 10 percent addition of Al_2O_3. A

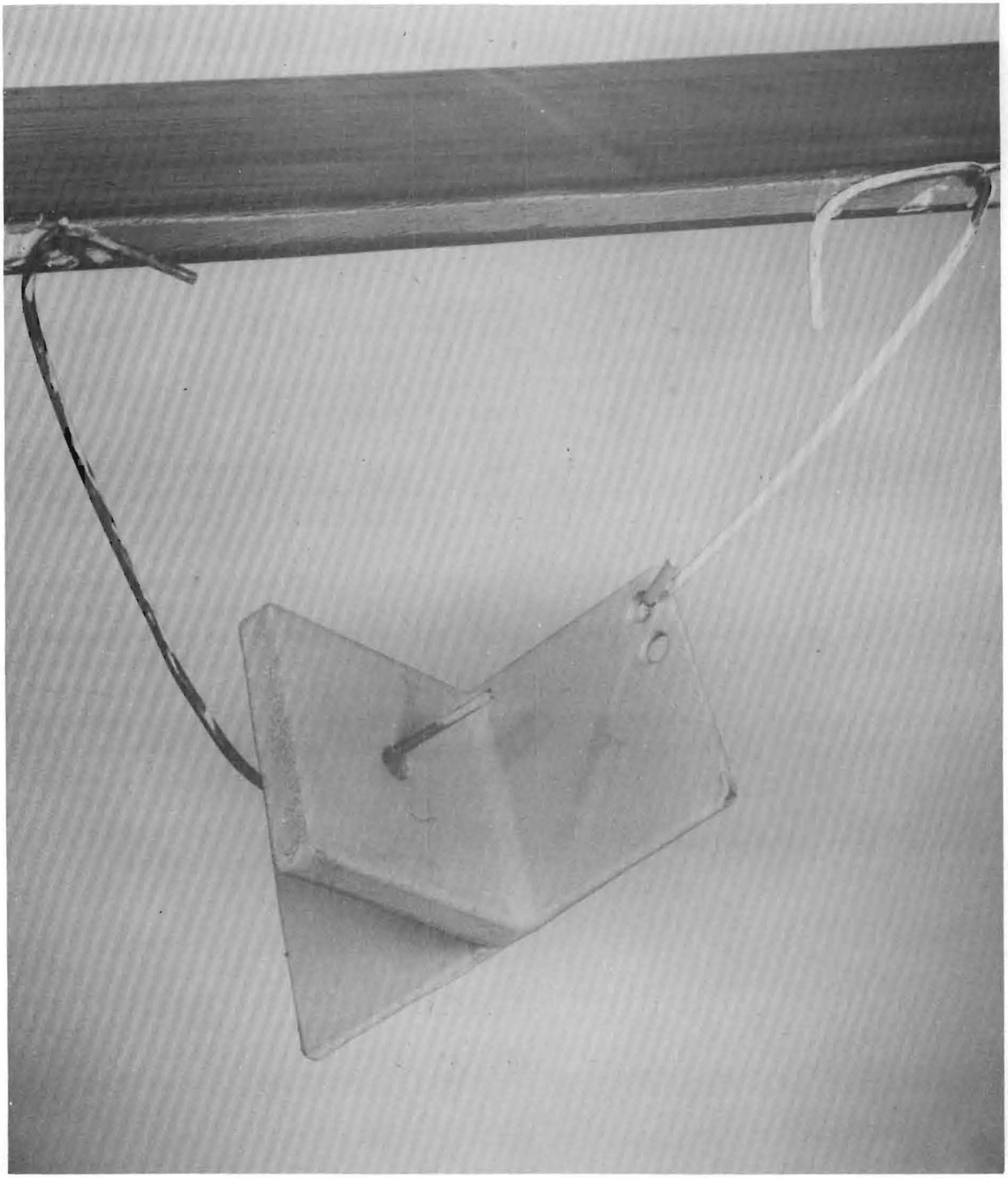

Figure 1. Method of Hanging T-Section for Draining.

satisfactory coating was obtained with an enamel made from Pemco frits and 7.5 percent Al_2O_3.

T-sections dipped with enamels containing 20 percent Al_2O_3 exhibited crawling and tearing along the edges of the 5/8-inch section and at the junction of the 5/8- and 3/16-inch section.

B. Thermal Shock Test

The steel used for fabricating the T-joint specimen was AISI C1012 which was secured in the form of 4- by 3/16-inch strip and a 4- by 5/8-inch flat.

The component pieces were welded and assembled according to the methods used in Contract No. NObs 66521 except that welding was accomplished by the manual arc method utilizing a GE 6WD 33B1 DC welder using reverse polarity.

Cleaning was accomplished by sandblasting and enamel was applied by dipping. Firing was on an open rack in the furnace with no special atmosphere used. Firing temperature was 1475° F for enamels containing 10 percent alumina and 1425° F for the Pemco enamel containing 7-1/2-percent alumina. Thermal shock tests were conducted on the T-sections according to the schedule of Mil-P-16961B. Tests were conducted with enamels of the Ferro Corp., the O'Hommel Co. and Chicago Vitreous Corp. containing 10 percent additions of alumina. The Pemco Corp. enamel had a 7-1/2-percent addition of alumina. Enamels from all four companies passed the 900° F shock test.

C. Hydrogen Extraction Studies

In an effort to obtain a quenching medium which would not react when steel was plunged into it at 1400° F, carbon tetrachloride was selected. Two samples of C1012 steel cut from the same stock were enameled and fired in an atmosphere of dry air for 22 minutes at 1400° F. One sample was quenched in carbon tetrachloride and the second sample was allowed to cool slowly in air. The sample quenched in carbon tetrachloride gave 0.41 mls of gas and the air cooled sample gave only 0.05 mls of gas. Since quenching is used to entrap the hydrogen by rapidly cooling the enameled specimen while the coating remains essentially intact, it was decided that water would continue to be used as the quenching medium.

To determine if rusting on drying is a factor in hydrogen extraction, two samples were enameled with the same enamel. One sample was allowed to dry in the open. The second sample was immediately put in the dryer after spraying and dried at 110° C. Both the samples gave 0.50 mls of gas, indicating that drying time was not a factor in gas extraction.

Firing for all hydrogen extraction tests was in the inconel chamber shown in Figure 5 in Summary Report No. 1, Project A-204, Contract No. NObs 66521 (July 31, 1955). This chamber was modified by sealing the holes in the side of the box and drilling two 1/2-inch holes in the center of the top of the chamber. A 1/4-inch stainless steel pipe was cut and welded into a rectangular shape to fit the inside dimensions of the bottom of the chamber. In the center of one side of the pipe on the long dimension of the rectangle a short piece of pipe was welded and threaded, and passed through a hole in the side of the box. One-sixteenth-inch holes were drilled on one-inch centers in the side of the 1/4-inch pipe at an angle of 45° below horizontal and facing the center of the box. A flexible stainless steel tube was attached to the threaded pipe to supply any atmosphere desired in the chamber.

The wet atmosphere firings were provided by passing air at a rate of 8 liters per minute through water at 25° C and then through the flexible stainless steel tube into the firing chamber.

The dry atmosphere firings were provided by passing air at 8 liters per minute through a calcium sulfate drying tube and then through sodium hydroxide flakes.

Samples were placed in the chamber supported on racks from 4-mesh stainless steel screens. The top was placed on the chamber and the atmosphere being used was pumped into the chamber for 10 minutes before placing the chamber in the furnace. Firing time for all tests was 22 minutes and the temperature was 1400° F.

After taking the chamber from the furnace, the lid of the chamber was quickly removed and the extraction samples immediately plunged into cold water. The samples were removed from the water, sandblasted and set up in the hydrogen extraction apparatus as shown in Figure 2. Hydrogen extraction procedure was the same as in Project Report No. 1, Project No. A-308, Contract No. NObs 72209, Bureau of Ships Code 312, Department of the Navy, except that butyl phthalate was added to the extraction chamber and a second vacuum pulled on the system before placing the gas burette on the chamber. It was found that the butyl phthalate would pick up air on standing and give erroneous readings on extractions if this air was not removed.

Tests with AISI C1012 steel have been completed with all four enamels containing 0 to 20 percent Al_2O_3. Table I gives the results of these tests.

Figures 3 and 4 show the effect of mill additions of Al_2O_3 on the amounts of gas extracted from the metal. Since temperature and firing time were constant the only variables were the Al_2O_3 and the firing atmosphere.

The variance with atmosphere seems to be greater for the high percentage Al_2O_3 enamels. The amount of gas given off by enamels containing no Al_2O_3

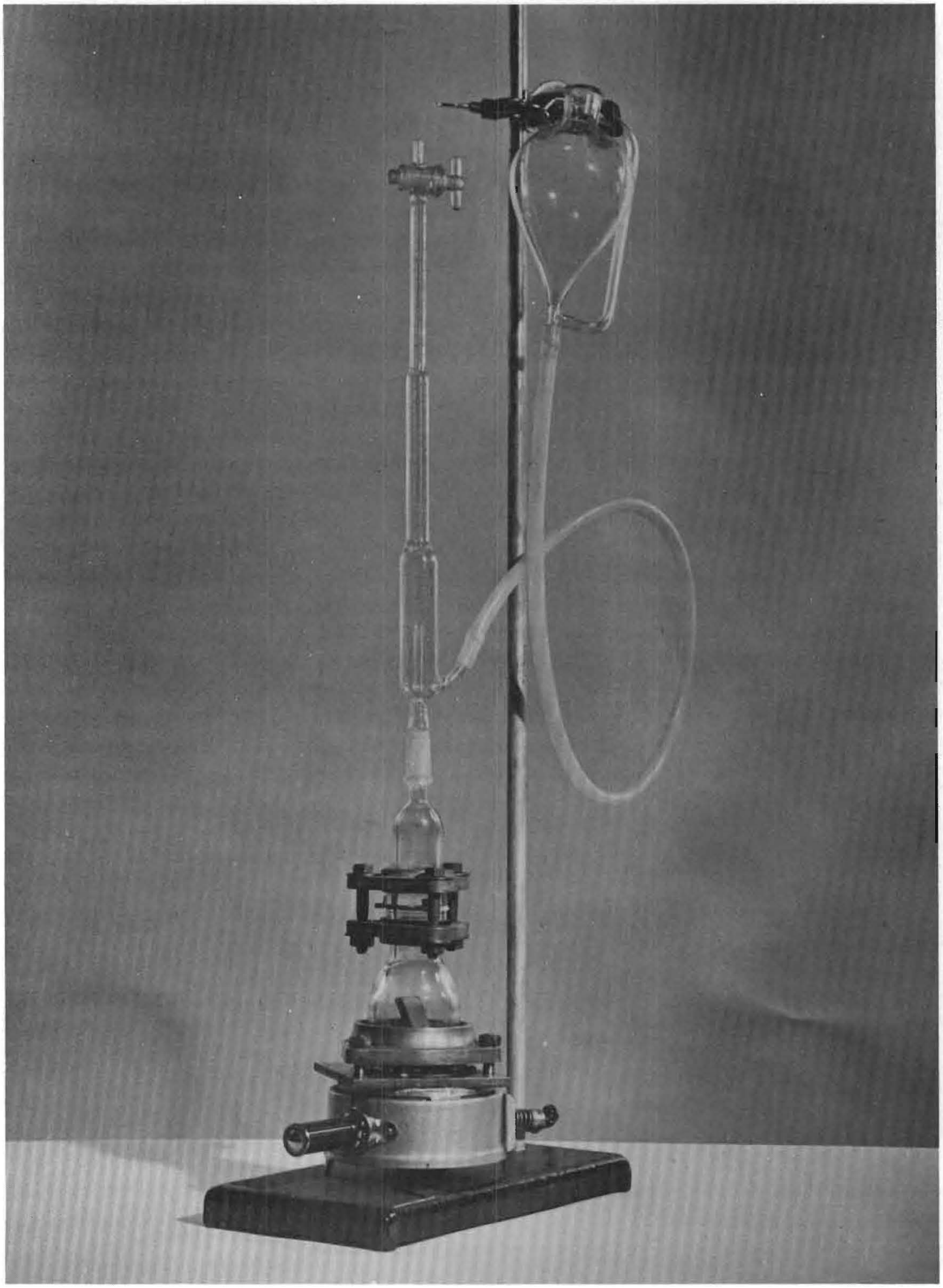

Figure 2. Hydrogen Extraction Apparatus.

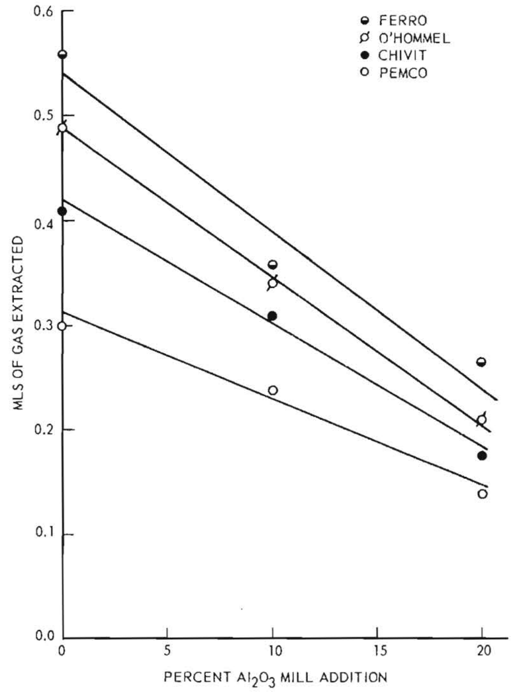

Figure 3. Hydrogen Extracted for Wet Atmosphere Firings.

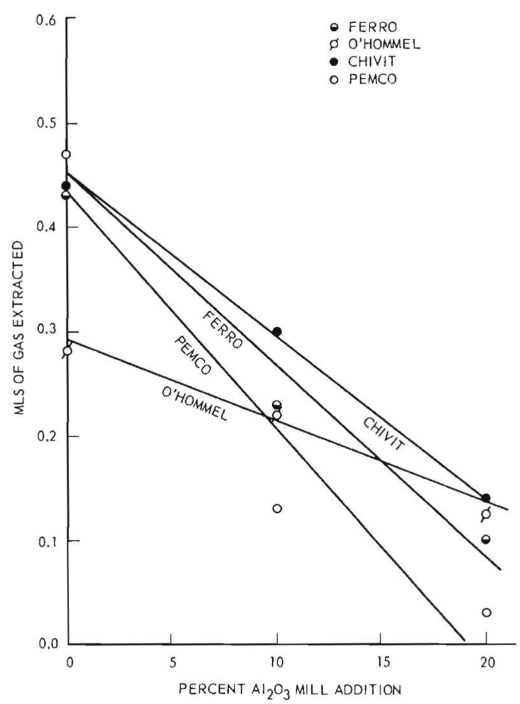

Figure 4. Hydrogen Extracted for Dry Atmosphere Firings.

did not seem to vary greatly with the firing atmosphere, but enamels containing 20 percent Al_2O_3 gave off a much smaller quantity of gas in a dry atmosphere. This may be due to gas escaping through the structure of the enamel upon cooling.

TABLE I

HYDROGEN EXTRACTED FROM AISI C1012 STEEL

Enamel	Al_2O_3 (%)	Atmosphere: Wet (mls of gas)		Atmosphere: Dry (mls of gas)	
Pemco	0	0.31	0.29	0.50	0.43
Pemco	10	0.28	0.21	0.13	0.13
Pemco	20	0.16	0.11	0.05	0.01
Ferro	0	0.60	0.52	0.55	0.30
Ferro	10	0.44	0.29	0.28	0.18
Ferro	20	0.30	0.18	0.15	0.05
Chivit	0	0.41	7.50	0.45	0.43
Chivit	10	0.37	0.25	0.32	0.28
Chivit	20	0.19	0.16	0.16	0.13
O'Hommel	0	0.50	0.48	0.28	0.28
O'Hommel	10	0.39	0.30	0.21	0.23
O'Hommel	20	0.20	0.32	0.08	0.15

D. Adherence

The adherence tests used on Contract No. NObs 66521 are being used for this work.

The sample size selected for use in this test was 2 by 9 by 3/16 inch. After sandblasting, the specimen was ground coated, by spraying, and then dried. Before firing, 3 inches of enamel were brushed from each end, leaving a 3-inch strip in the center undisturbed.

After firing, an extensiometer which was constructed for this test was attached to the specimen on each side of the enamel strip. The entire assembly was then set up in a Riehle 60,000-lb Universal testing machine.

Stretching of the piece was begun and was continued until the extensiometer indicated 6 percent elongation of the desired 3-inch test area in the center. Adherence count was determined by a PEI adherence meter. Figure 5 shows curves on adherence studies of a C1012 steel. With the Pemco, Ferro and Chivit enamels maximum adherence was obtained with a 10 percent addition of Al_2O_3, but with the enamel secured from the O'Hommel Co., maximum adherence was obtained with a 20 percent addition of Al_2O_3.

E. Oxidation Studies

A representative number of 2- by 2-inch samples of C1012 steel were sandblasted and cleaned with alcohol. These samples were weighed to the fourth decimal place on an analytical balance. The samples were placed on wire racks at various spots in the inconel chamber used for hydrogen extraction. Dry air was pumped into the chamber at a rate of 8 liters per minute for 10 minutes before placing the chamber in the furnace at 1400° F for 22 minutes. The air was allowed to run throughout the heating and cooling cycle of the chamber. The chamber was cooled to room temperature before removing samples from the chamber. Samples were reweighed to determine the weight of oxide gained. Tests were run with dry air, moist air and carbon dioxide. All results were reproducible within 5 percent.

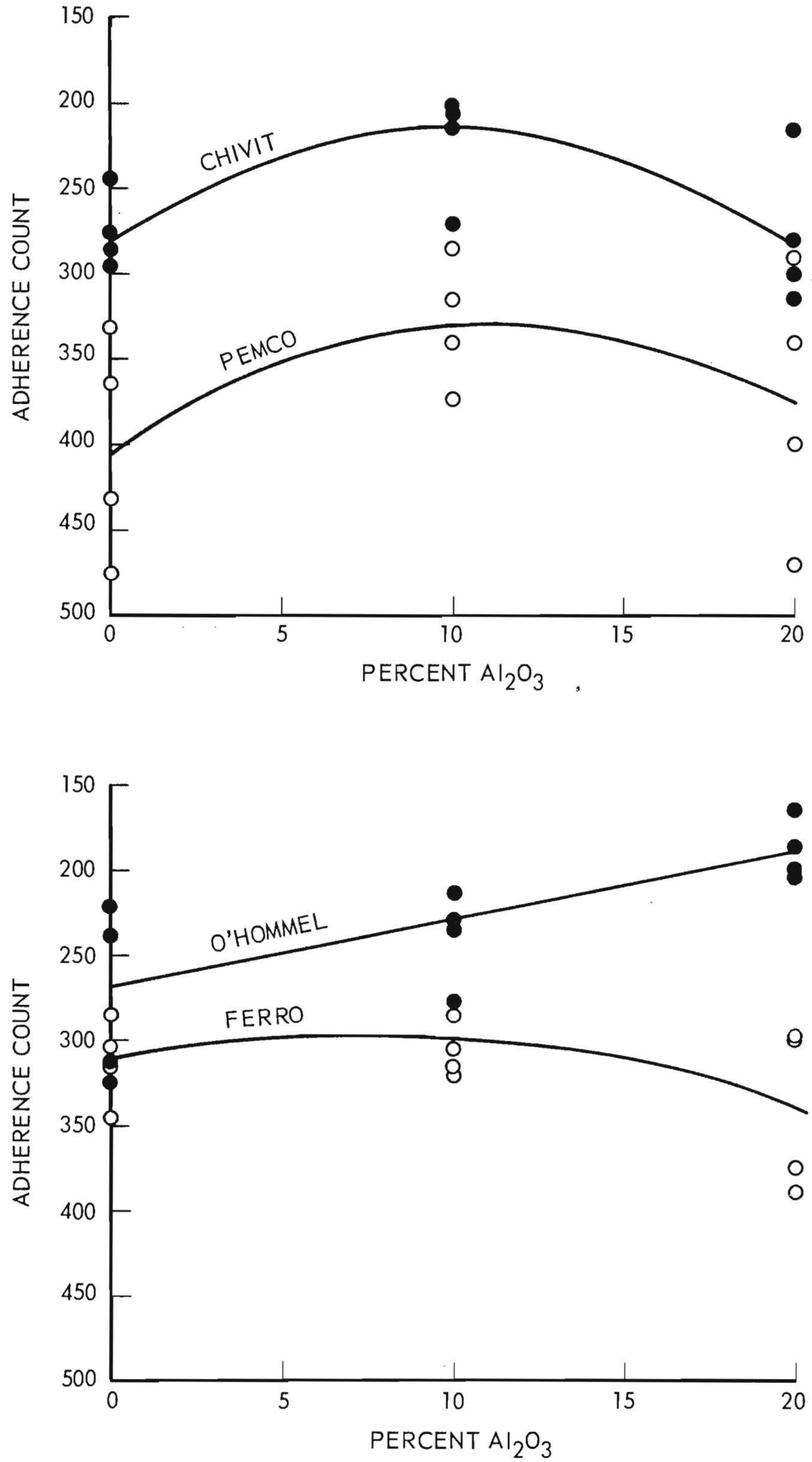

Figure 5. Percent Al_2O_3 Versus Adherence Count.

Five steels with carbon contents of 0.04, 0.12, 0.19, 0.27, and 0.36 percent were selected for oxidation studies. Two samples of each steel were sandblasted, cleaned, weighed, fired and reweighed to determine the amount of oxide gained. The procedure used was the same as that used in determining the reproducibility of results. Tests were run with wet and dry atmospheres. Figure 6 and Table I show the results of these oxidation studies. Oxidation decreases as carbon content increases. Also, limits of reproducibility tend to improve with increase in carbon content.

TABLE II

OXIDATION STUDIES ON STEELS CONTAINING VARYING PERCENTAGES OF CARBON

	Air--Dry Atmosphere		Air--Wet Atmosphere		CO_2 Atmosphere	
Carbon Content (%)	Wt of Steel (g)	Wt of Oxide (g)	Wt of Steel (g)	Wt of Oxide (g)	Wt of Steel (g)	Wt of Oxide (g)
0.04	102.0000	0.0615	103.0824	0.0803	104.1344	0.0457
0.04	104.0487	0.0703	101.3974	0.0701	103.5472	0.0539
0.12	92.4239	0.0594	91.6513	0.0710	88.8455	0.0714
0.12	95.0757	0.0714	90.3387	0.0768	92.2564	0.0709
0.19	97.1413	0.0534	96.8762	0.0458	100.9295	0.0619
0.19	98.4487	0.0539	98.3658	0.0579	101.1637	0.0494
0.27	95.1681	0.0521	95.4764	0.0576	101.2188	0.0598
0.27	93.5560	0.0422	95.4652	0.0547	93.8086	0.0612
0.36	98.9100	0.0390	99.1418	0.0306	92.2564	0.0825
0.36	98.9653	0.0422	101.0046	0.0408	101.2330	0.0626

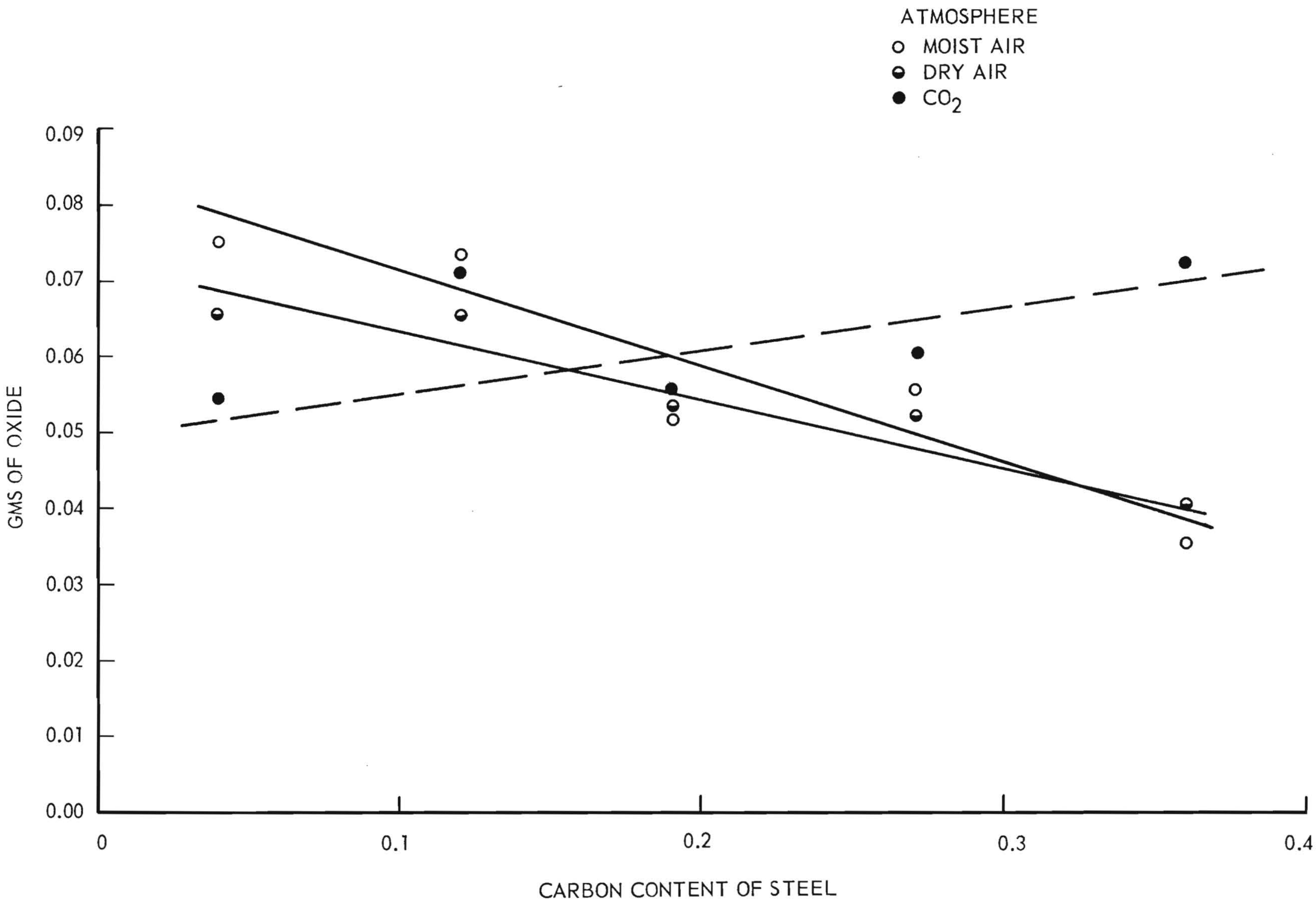

Figure 6. Oxidation Versus Carbon Content of Steel.

F. Wettability Studies

Pellets were made from each of the four enamels and from compositions of the enamels containing 10 percent Al_2O_3. The enamel slips were dried and the dry enamels pressed into pellets with a 3/4-inch die. Three grams of enamel and four drops of water were used to press each pellet at a pressure of 8000 psi. The pellets were placed on 2- by 2-inch sections of metal cut from steel ranging from 0.04 to 0.36 percent carbon which had been previously sandblasted. Two samples of each steel were run with each enamel in both wet and dry atmospheres. Firing was the same as for oxidation. The spread of the pellet served as a measure of the wettability of the metal. The limits of reproducibility were greater than the spread of the enamel in various steels and the difference of spread in various enamels.

G. Enamel Defects

Early in the project attempts were made to cause all four enamels to fish-scale. Enamels were fired in an atmosphere containing 100 grams of water per cubic foot. The Ferro enamel developed a few shiner scale but the other enamels would not fish-scale even after being heated to 110° C for one week, except for a very few shiner scale. Fish scales were developed on the O'Hommel enamel only after forcing atomic hydrogen through the metal using the hydrogen diffusion apparatus described in project A-204, Contract NObs 66521.

A new supply of all frits and of clay #540 (O'Hommel) was ordered when the old supply was exhausted. Metal sprayed with the new batches of enamel fish-scaled severely almost immediately upon cooling. Mill additions of 10 percent Al_2O_3 caused a lessening of fish scale but did not completely stop it. Additions of 20 percent Al_2O_3 stopped fish-scaling. Investigations to determine the cause of enamel defects in the new batch of materials showed the enamel structure to be changed.

Four- by four- by three-sixteenths-inch C1012 steel plates were cut and one plate each was sprayed with both old and new batches of enamel from Ferro Corp., Chicago Vitreous Corp., and the O'Hommel Co. The six plates were fired at the same time in the inconel chamber with a wet atmosphere for 22 minutes at 1375° F. All new batches of the three enamels fish-scaled severely on cooling. The old Ferro enamel developed a few shiner scale and the old Chivit and O'Hommel enamels failed to develop fish scale. Investigation of the enamel under the microscope showed the bubble film of the old enamels to be much larger than the bubble film of the new batch of enamels.

In the case of the O'Hommel enamel the frits used for the new batch of enamel were taken from the old supply of frits. For the Chivit and Ferro enamels the new supply of frits had to be used. For all three enamels it was necessary to use the new supply of O'Hommel's #540 clay. For the six test plates fired in the inconel chamber fineness and specific gravity of all enamels were 1.7 and the coatings applied to the 3/16-inch plate were the same thickness. The six 3/16-inch plates were cut from the same strip of AISI C1012 steel, and were fired together for the same length of time. Therefore, the only variable was the new supply of the O'Hommel Company's #540 clay.

Figures 7, 8, 9, 10, 11, and 12 show the difference in bubble film between old and new batches of the three enamels.

It is generally accepted that bubble film is an important factor in determining whether or not an enamel will fish-scale when applied to a metal.

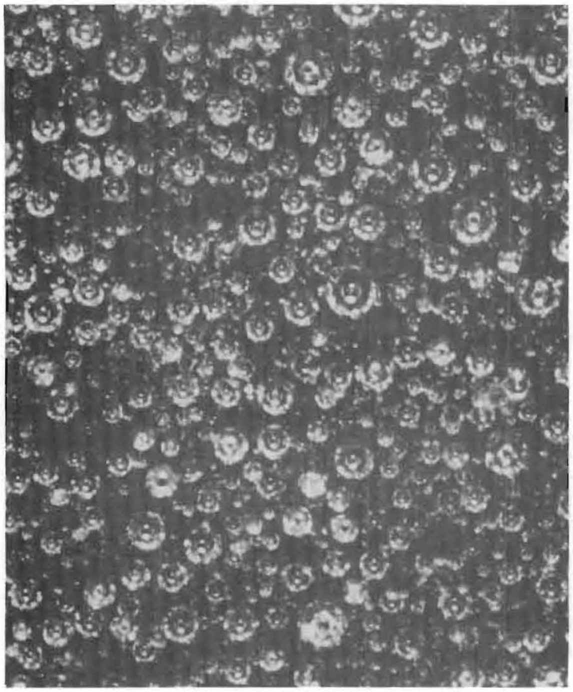

Figure 7. Bubble Film of Old Batch of Chivit Enamel (60X).

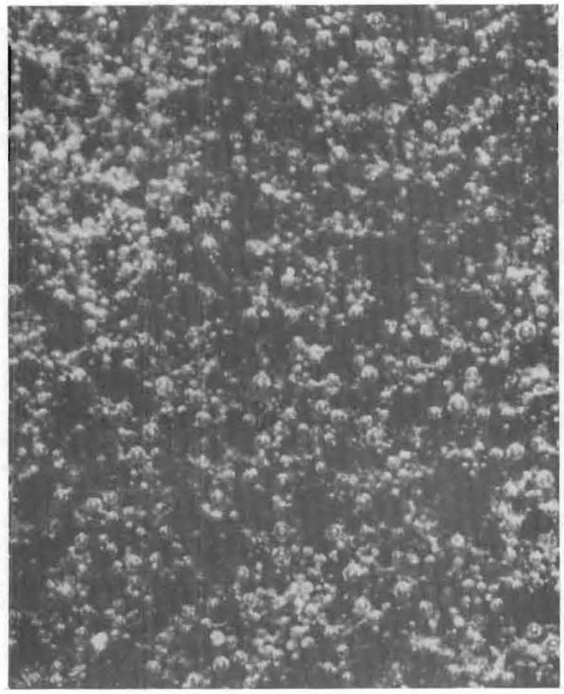

Figure 8. Bubble Film of New Batch of Chivit Enamel (60X).

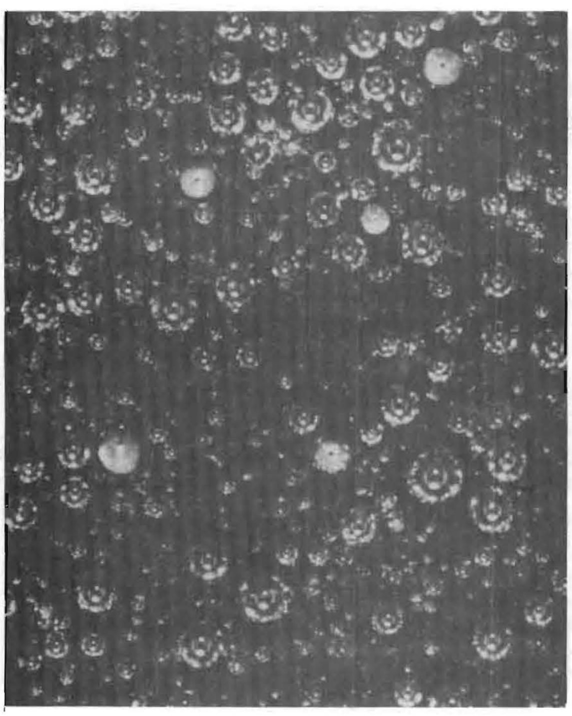

Figure 9. Bubble Film of Old Batch of Ferro Enamel (60X).

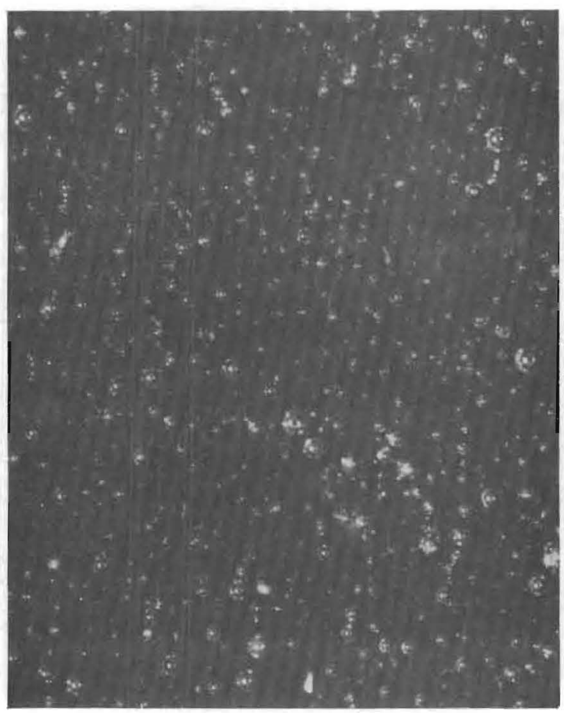

Figure 10. Bubble Film of New Batch of Ferro Enamel (60X).

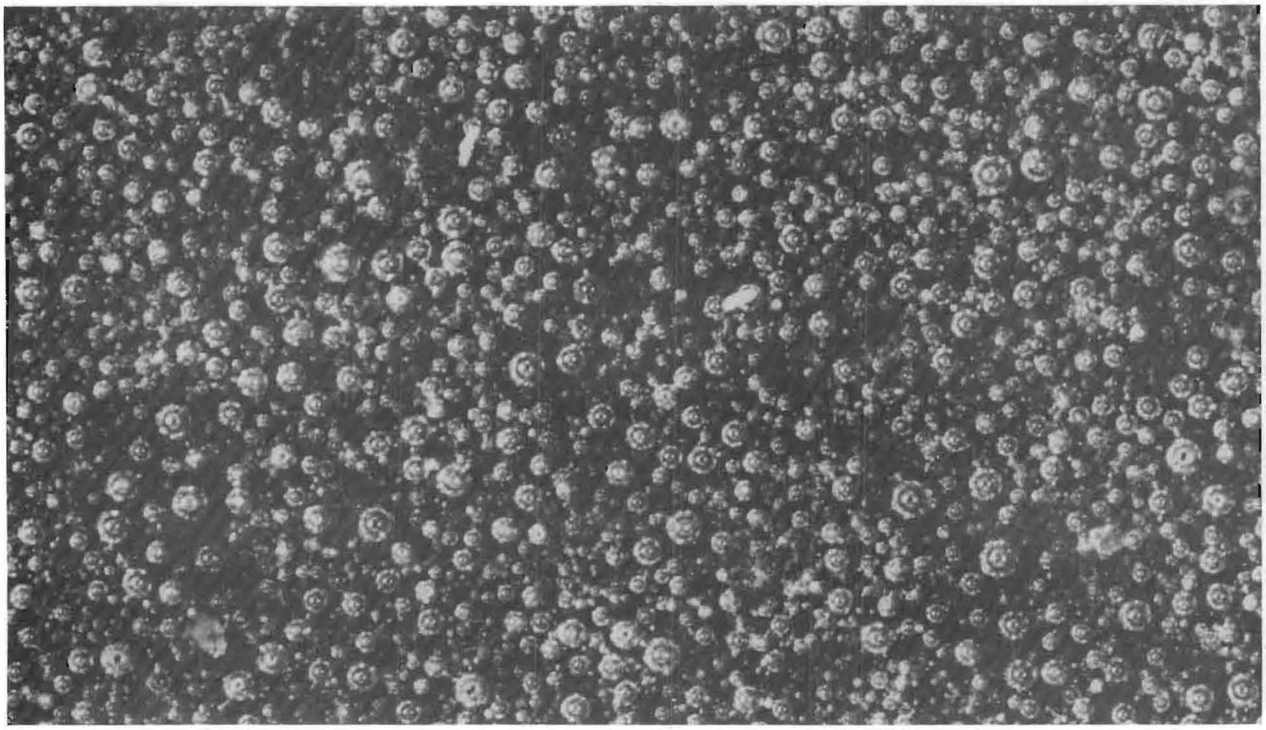

Figure 11. Bubble Film of Old Batch of O'Hommel Enamel (60X).

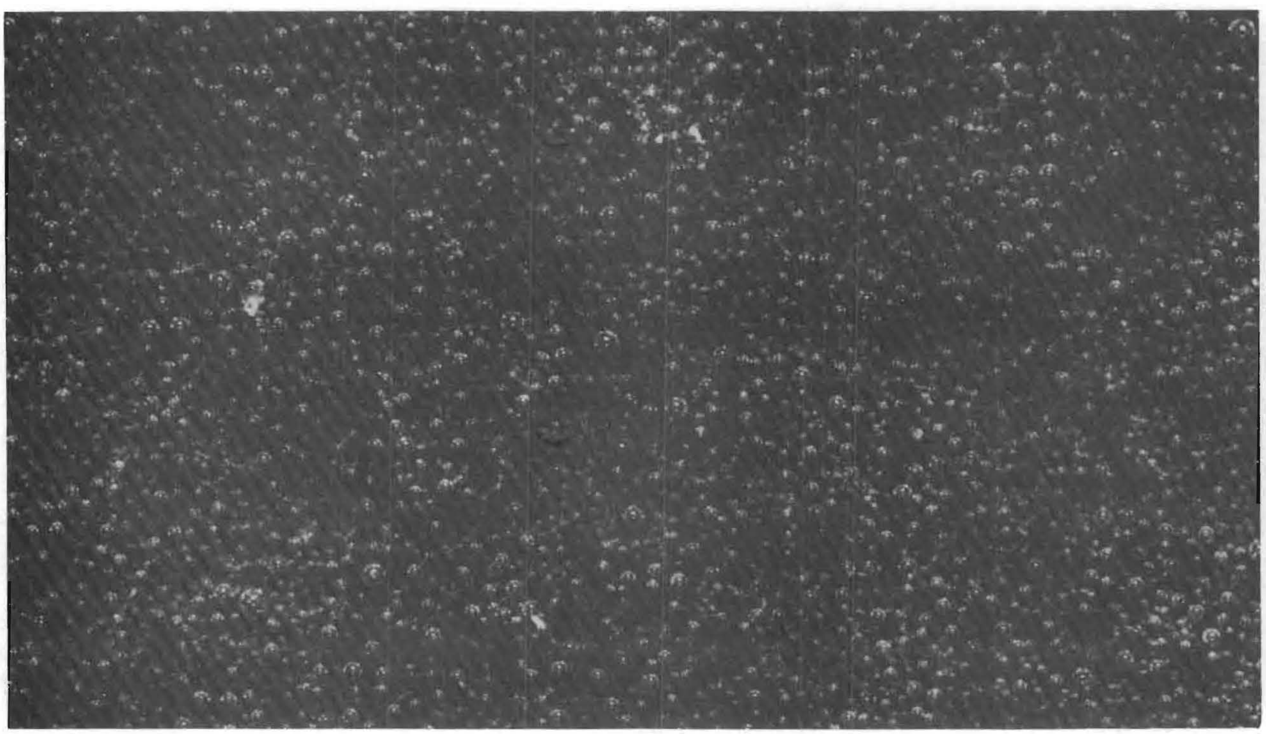

Figure 12. Bubble Film of New Batch of O'Hommel Enamel (60X).

This work shows that bubble film and tendency to fish-scale cannot be determined from batch to batch of enamels even when raw materials are provided by the same manufacturer. It has also been previously shown that bubble film is largely dependent on firing time and temperature; therefore, a more reliable method of controlling enamel defects is needed.

A better method of controlling enamel defects would not depend on bubble film of the enamel. Small additions of Al_2O_3 have shown a tendency to reduce fish scale and larger additions have completely eliminated it. At the same time Al_2O_3 additions have improved the adherence of the enamel. Future work will be directed toward mill additions of Al_2O_3 and other substances as a substitute for the effect of bubble structure.

IV. FUTURE WORK

Present plans call for hydrogen extraction and adherence tests to be run on steels with carbon contents from 0.05 to 0.36 percent.

Investigations of effects of mill additions on enamel in relation to fish-scaling and adherence will be studied. Efforts will be directed toward finding a substitute for bubble film.

Respectfully submitted:

J. D. Walton
Project Director

J. N. Harris
Research Assistant

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SUMMARY REPORT NO. 2

PROJECT NO. A-308

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON and J. N. HARRIS

- o - o - o - o - o -

CONTRACT NO. NObs 72209
INDEX NO. NS 061-087
BUREAU OF SHIPS, CODE 312
DEPARTMENT OF THE NAVY

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SEPTEMBER 1, 1957

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I. SUMMARY

1 Hydrogen extraction tests were completed on steels having a carbon content range of 0.04 to 0.44 per cent. These tests were run on enamels received from the following manufacturers: The Pemco Corporation, Ferro Corporation, Chicago Vitreous Corporation, and the O. Hommel Company. Tests were also run on the above enamels after mill additions of calcined alumina.

2 Evaluation of the factors responsible for bubble structure reveals the need for finding a more reliable substitute for the effects of bubble structure.

3 An evaluation of mill addition studies shows that calcined and fused alumina are the two most valuable mill additions for this work.

4 Metal studies show that an increase in carbon content causes an increase in fishscale. These studies also show that enamels can be formulated which will minimize the effect of carbon content on fishscale.

5 Large mill additions have reduced fishscaling tendencies, but tearing and hairlining studies have caused a re-evaluation of these additions. This study shows that additions of 10- to 20-per-cent fused alumina give the best results.

6 Adherence tests (flexibility) show all enamels tested have sufficient flexibility, so that this attribute does not constitute a major problem.

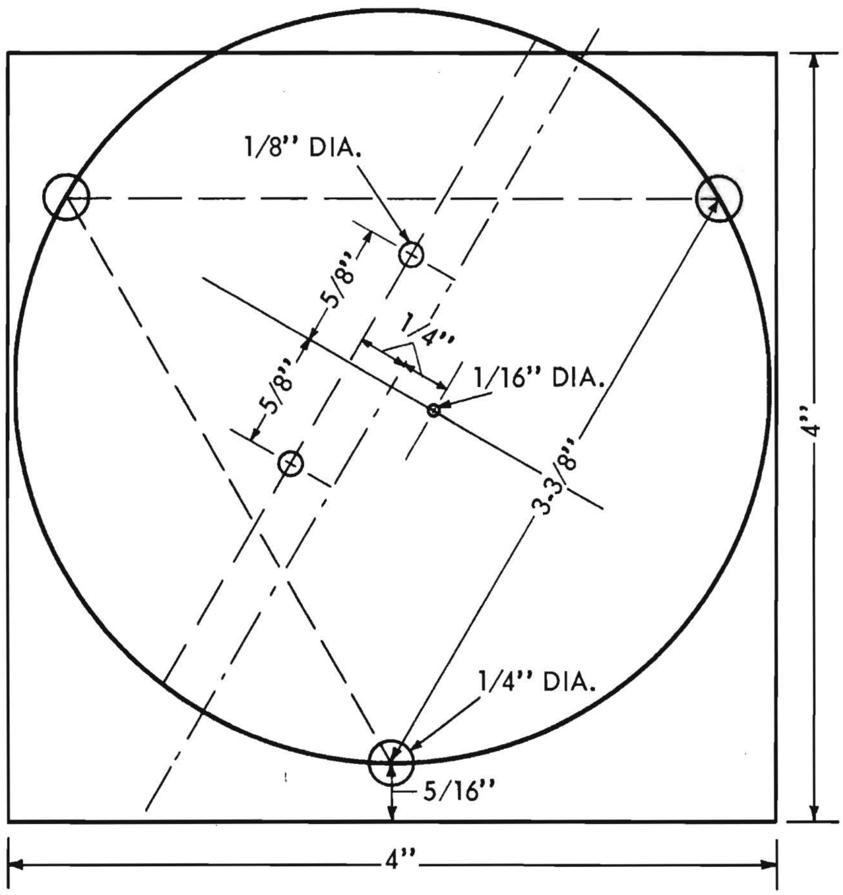
7 Welding studies show that enameling of welds is more a problem of selecting the right enamel than of weld technique or electrode used. Welds with enamel defects can be produced through the improper selection of weld electrode and porcelain enamel, but welding technique is not an important factor in that welds containing cavities are more receptive to porcelain enamel than sound welds. Proper selection of welding electrode and enamel will obviate most defects.

ERRATUM

Project Report No. 1, Project No. A-308: Page 2, Part C, Paragraph 2.

Change to:

On a chord drawn through any point 1/4 inch from the center of the circle described by the studs, and drawn perpendicular to a line connecting that point and the center of the circle, two 1/8-inch diameter holes were drilled, each 5/8 inch from the perpendicular. On the opposite side of the center from the chord, a 1/16-inch diameter hole was drilled 1/4 inch from the center.



Construction of Base Plate for Hydrogen Extraction Apparatus.

8 Thermal shock studies indicate that enamels can be formulated which will pass the present shock test on any metal.

9 Efforts are being made to develop a new thermal shock test more similar to actual shocks encountered in service.

II. INTRODUCTION

10 This project was initiated on October 31, 1956 and has as its objectives:

a. To develop a complete and technically accurate description of steel plates acceptably receptive to porcelain enamel coatings. This description is to be incorporated into material specifications for Government procurement,

b. To determine the factors which affect the enameling characteristics of steel plates and welds,

c. To establish the validity of parameters and set limits for control of quality for enamelability of steel plates and welds, and

d. To assess the factors responsible for defectively coated parts intended to conform to Specifications Mil-P-16961.

III. EXPERIMENTAL PROGRESS

A. Hydrogen Extraction

11 Extraction tests were completed on steels having a carbon content range of 0.04 to 0.44 per cent. These tests were run with enamels received from the Pemco Corporation, Chicago Vitreous Corporation, Ferro Corporation and the O. Hommel Company. Tests were also run on each of the above four enamels after 10-per-cent additions of calcined alumina. These tests were run in the manner described in Project Report No. 1. Table I shows that a 10-per-cent addition

TABLE I

HYDROGEN EXTRACTED FROM STEEL

(3/16-INCH PLATE THICKNESS)

Carbon Content of Steel	Pemco Enamel	Pemco Enamel with 10% Alumina	Chivit Enamel	Chivit Enamel with 10% Alumina	Ferro Enamel	Ferro Enamel with 10% Alumina	O. Hommel Enamel	O. Hommel Enamel with 10% Alumina
0.04	0.20	0.03	0.00	0.25† (.40 .10)	0.20	0.47††	0.27† (.10 .44)	0.06
0.12	0.46	0.13	0.39	0.30	0.42†	0.23	0.28	0.22
0.19	0.12	0.03	0.04	0.10	0.03	0.50 (.67 .35)	0.16	0.27
0.27	0.25††	0.22††	0.51††	0.07††	0.42††	0.05††	0.60††	0.10††
0.44	0.32	0.22† (.39 .05)	0.18 (.30 .06)	0.10	0.40	0.22 (.40 .05)	0.26	0.12

Note: Two samples were run for each enamel, except as indicated, with maximum variation between samples being 0.15.

†Variation greater than 0.15. Number in parenthesis shows variation.

††One sample only.

of alumina causes a decrease in the amount of gas extracted. The above enamels, containing 20-per-cent mill additions of calcined alumina, were applied to C1012 steel. These samples had an even smaller amount of gas extracted than the enamels containing 10-per-cent additions of alumina.

12 It can be seen from Table I that there is no definite relationship between carbon content of steel and the amount of gas extracted. Tests were limited by the amount of steel available. At the present time large amounts of steel in various grades are being obtained to further this work.

B. Bubble Film and Mill Addition Studies

13 As noted in previous reports, the size of the bubbles in the bubble stratum would seem to be the controlling factor as to whether an enameled plate will fishscale. Three enamels were made with O. Hommel frits, substituting Ferro's Green Label Clay, Red Label Clay and Black Label Clay for the O. Hommel No. 540 clay. These enamels were sprayed on 3/16-inch C1012 steel plates and fired in a wet atmosphere. The plates coated with the enamel made with Green Label Clay had large, well spaced bubbles in the bubble stratum and, as expected, very few fishscales. The enamel containing Red Label Clay had smaller bubbles than the previous plate and had more fishscale. The enamel made with Black Label Clay had very small bubbles and fishscaled severely.

14 Many factors, such as firing temperature, firing time, grinding fineness, and thickness of coating, enter into the formation of bubble structure. Each of these factors was investigated on each enamel and the optimum established and used in each. Other variations of the common mill additions such as bentonite, magnesium carbonate, and silica, were made. None of the above factors, however, influenced the formation of bubble structure as much as the

type of clay used. The effect of clay was described in Summary Report No. 1, which shows photographs of the same enamel made with two different batches of the same clay. This points up the need in enamels for a substitute for the effect of bubble structure, such as mill additions of alumina. Photographs of these effects can be seen in Figures 22 and 23 of Annual Report No. 1, Contract No. NObs 66521, wherein it was indicated that an alumina particle functioned as a bubble in contributing to thermal shock resistance.

15 Studies were made of the effects of the following mill additions: clay, silica, calcined and fused alumina, feldspar, and pyrophyllite. In all cases the following enamel formulation was used:

100 parts frit
6 parts clay
4 parts silica
1/2 borax
1/8 bentonite
1/8 magnesium carbonate
50 water.

All mill additions were either additions to or variations of this formula. As noted in Summary Report No. 1, a change in quality of a new lot of O. Hommel No. 540 clay caused a change in bubble structure in fired enamels and a change in tendency to fishscale. At a later date a new supply of Chicago Vitreous No. 259 frit was ordered. This frit was found to be obsolete and had been replaced by their No. 289. The enamels made with this frit did not act in the same manner as the enamel made with the old supply of frit. Frit and clay are variables in quality affecting coating properties. In order to standardize a mill batch formula it would seem, for purposes of government procurement, essential to standardize on a frit smelt batch formulation controlled by an independent means and have a quantity of such frit on hand at a Naval laboratory or readily available from the National Bureau of Standards. A standard test procedure for clay involving use of the standard frit appears necessary.

16 The clay content of an enamel was varied from one to nine parts clay, keeping all other components the same. Fishscaling decreased gradually and bubble size increased up to six parts clay. Above six parts clay, fishscaling continued to decrease; however, bubble spacing increased up to abnormally wide separation, and the bubble structure began to have the appearance of one to which additions of alumina had been made.

17 Mill addition studies were made by varying the silica content from 0 to 30 parts silica. Less than four parts silica gave an acceptable bubble structure if fired at the proper temperature; however, the firing range was very narrow. Ten parts silica gave a fairly well developed bubble structure, a much wider firing range, and very little fishscale. Twenty parts silica gave no fishscale, but had small bubbles in the bubble structure. Thirty parts silica gave no fishscale but had very few and very fine bubbles in the bubble strucure. Further pursuit of the silica variation study was discontinued because the enamels thus produced were of poor fit and therefore believed to have poor resistance to thermal shock.

18 Mill additions of feldspar were also made but very little difference was discernible between additions of 10, 20 and 30 parts.

19 Mill additions of 10, 20 and 30 parts pyrophyllite were tried but blistering and bubbling of the coating caused this work to be discontinued.

20 Mill additions of calcined and grain aluminas still seem to give the best results. This work indicates that further efforts need to be placed on the particle size of the mill additions.

21 Tearing, thermal shock and adherence tests were run on all of the above mentioned mill addition enamels and are discussed later in the report under their respective sections.

C. Metal Studies

22 Plates ranging in carbon content from 0.04 to 0.44 per cent were enameled with two enamels, one which gave only slight fishscaling on C1012 steel and the other which fishscaled severely on C1012 steel. With either enamel, fishscaling increased as carbon content increased.

23 A second test was run on six different steels ranging in carbon content from 0.05 to 0.24 per cent. These steels were coated with a number of different enamels. Table II shows the results of enamels tested. Table III shows the heat history of steels used. In this test, with all enamels that were borderline cases (those that fishscale on only certain plates) an increase in fishscale was noted with an increase in carbon content. This table also shows that fishscaling can be controlled by the type of enamel applied.

24 All firing for this test was done in a closed chamber into which an atmosphere of moist air was pumped at a rate of 8 liters per minute. The moist air was provided by passing air through water at room temperature. This gave conditions very favorable to producing fishscale.

D. Tearing Studies

25 To determine tearing and hairlining properties of enamels, the following test was used. The test plate was composed of two pieces of 14-gage enameling

TABLE II

TENDENCY TO FISHSCALE VERSUS CARBON CONTENT OF STEEL

Carbon Content of Steel	Pemco Enamel +20% Calcined Alumina	Pemco Enamel +10% Fused Alumina	Pemco Enamel +20% Fused Alumina	Chivit Enamel	Chivit Enamel +10% Calcined Alumina	O. Hommel Enamel +10% Fused Alumina	Ferro Enamel	Ferro Enamel +10% Calcined Alumina	Ferro Enamel +20% Calcined Alumina	Ferro Enamel +10% Fused Alumina	Ferro Enamel +20% Fused Alumina
0.05	yes	white specks	yes	yes	no	no	yes	yes	no	yes	no
0.07††	yes	white specks	white specks	yes	no	no	no	no	no	yes	no
0.07†	yes	white specks	white specks	yes	yes	no	yes	no	no	yes	no
0.16	yes	white specks	yes	yes	no	yes	yes	yes	no	yes	yes
0.19	yes	white specks	yes	yes	no	yes	yes	yes	no	yes	yes
0.24	yes	white specks	yes	yes	yes	yes	yes	yes	no	yes	yes

Note: These were the only enamels tested due to the short supply of steel. White specks in the Pemco enamel appeared to be fishscale.

†Hot rolled, pickled and oiled

††Capped steel

TABLE III

HEAT HISTORIES OF STEELS USED IN FISHSCALING
AND HYDROGEN EXTRACTION TESTS

Carbon	Mn	P	S	Si	Cu	Al	Source and Type
.05	.30	.015	.034	.015	.06	.039	U. S. Steel, Aluminum-killed
.07	.35	.009	.025	----	---	----	U. S. Steel, Capped
.07	.25	.009	.026	----	---	----	Inland, hot rolled, pickled and oiled
.16	.38	.012	.030	.06	.05	.009	U. S. Steel, silicon-semi-killed
.19	.47	.013	.028	----	---	----	Inland, hot rolled
.24	.43	.012	.024	----	---	----	Inland, hot rolled
.04	.37	.008	.030	.007	.10	.005	U. S. Steel, rimmed
.12	.40	.010	.031	----	---	----	Atlantic, hot rolled strip
.27	.47	.010	.029	.04	---	----	Inland, hot rolled sheet
.44	.79	.026	.025	.23	---	----	Inland, hot rolled sheet

quality, low-metalloid steel that was spot welded together. (See Figure 1.) The front plate was 5-1/2 inches by 8 inches, and the back plate was 2-1/4 inches by 5-1/2 inches. The test plates were pickled and nickel flashed. Slip consistency of enamels tested was controlled by carefully weighing all ingredients according to the batch formula listed in Section B of this Chapter and ground to a fineness of 6 to 8 grams retained on a 200-mesh screen when a 50-ml sample of slip was poured and washed through the screen. The specific gravity was adjusted to 1.7 by the addition of water. The ground coat enamel to be tested was then sprayed on the front of the test plate, dried and fired for five minutes at the optimum temperature for the enamel being used. The plate was allowed to cool,

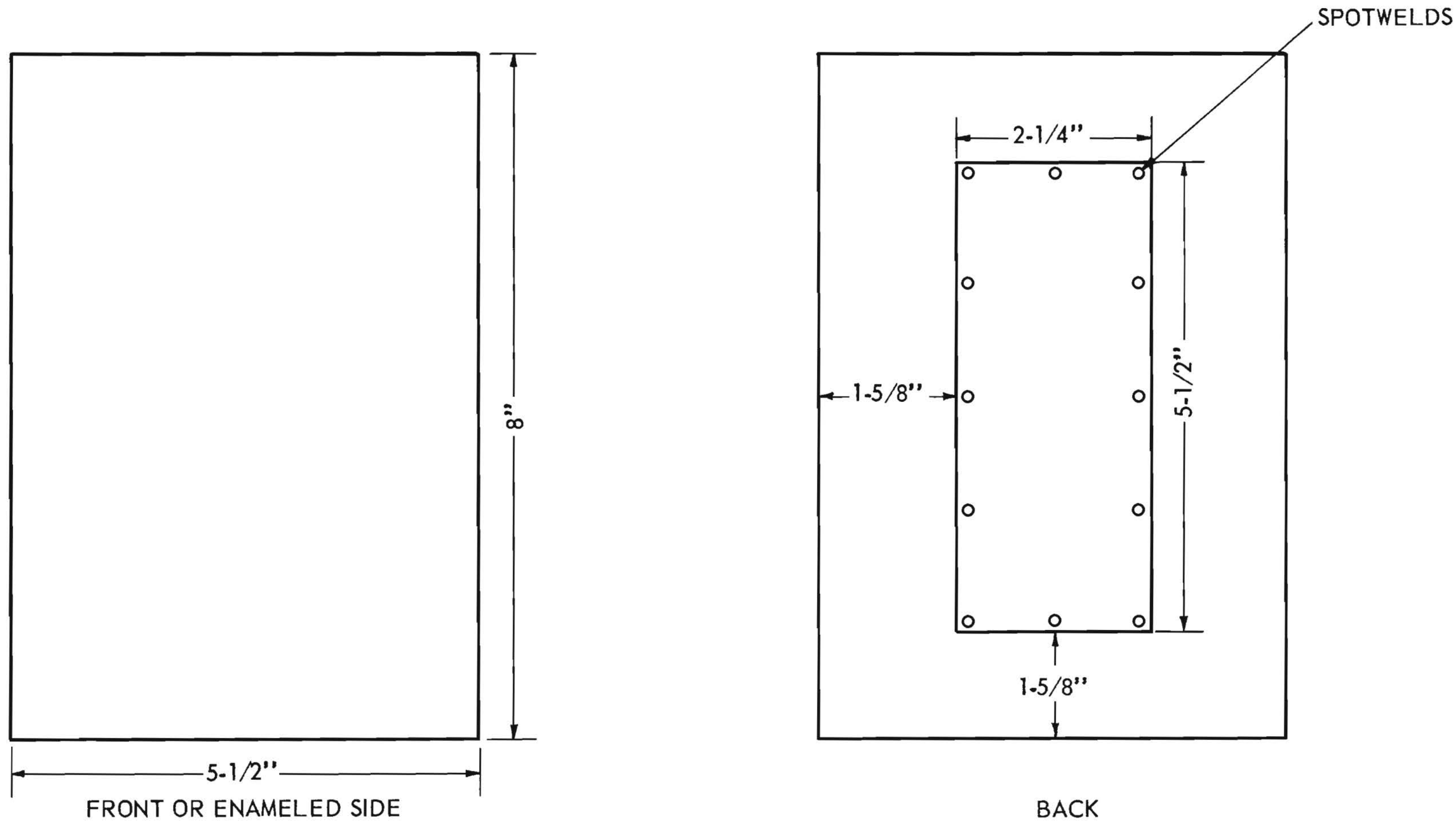


Figure 1. Tearing Test Sheet.

observed for tearing and then reheated to 1000° F for 10 minutes. The plate was allowed to cool, observed for hairlining and reheated to 1000° F for 10 minutes. After cooling, observations were again made for hairlining. Table IV shows the results of this test. It can be seen from the table that the best results were obtained with the enamels containing 10- and 20-per-cent fused alumina. The enamels containing 10-per-cent calcined alumina gave good results, but a problem of tearing developed at higher percentages. This had previously been seen when these enamels were applied to T-sections. Fused alumina is preferred over calcined alumina for this reason. Enamels containing only normal mill additions developed hairlines upon reheating. This possibly explains the reason that these enamels develop a "sandy feel" during thermal shock testing. The silica and feldspar additions had little effect on the tearing and hairlining properties of enamels.

E. Adherence Tests (Flexibility)

26 Adherence tests were run on an enamel containing mill additions of fused alumina, calcined alumina, silica and feldspar.

27 This test consisted of dropping a known weight a certain distance and indenting a 20-gage section of enameled metal. The amount of enamel chipped off the metal was measured by a Porcelain Enamel Institute Adherence meter.

28 This test was used only for determining the maturing range and firing conditions for all enamels being used in the other tests. Enamels were fired on 20-gage metal samples over a range of temperatures. Samples giving the highest adherence index were selected as having the proper firing temperature. Table V shows the results of this test.

TABLE IV

TEARING TESTS

Enamel	Initial Firing	First Reheat	Second Reheat
Pemco	No Defects	Hairlines	Hairlines
Pemco + 10% calcined alumina	No Defects	Hairlines	Faint Hairlines
Pemco + 20% calcined alumina	Bad Tearing	Bad Tearing	Bad Tearing
Pemco + 10% fused alumina	No Defects	Faint Hairlines	Faint Hairlines
Pemco + 20% fused alumina	No Defects	No Defects	Very Faint Hairlines
Ferro	No Defects	Very Faint Hairlines	Very Faint Hairlines
Ferro + 10% calcined alumina	No Defects	Hairlines	Hairlines
Ferro + 20% calcined alumina	Bad Tearing	Some Healing	No Change
Ferro + 10% fused alumina	Faint Tearing	Hairlines	Hairlines
Ferro + 20% fused alumina	Change in Color	Faint Hairlines	Faint Hairlines
O. Hommel	No Defects	Hairlines	Hairlines and Slight Tearing
O. Hommel + 10% calcined alumina	Slight Tearing	Slight Tearing	Slight Tearing
O. Hommel + 20% calcined alumina	Bad Tearing	Some Healing	No Change
O. Hommel + 10% fused alumina	Slight Tearing	Hairlines	Hairlines
O. Hommel + 20% fused alumina	Slight Tearing	Faint Hairlines	Faint Hairlines
Chivit	No Defects	Hairlines	Hairlines
Chivit + 10% calcined alumina	Slight Tearing	Tearing and Hairlines	Tearing and Hairlines
Chivit + 20% calcined alumina	Bad Tearing	Some Healing	No Change
Chivit + 10% fused alumina	Faint Tearing	Faint Tearing	Faint Tearing
Chivit + 20% fused alumina	No Defects	No Defects	No Defects
Chivit + 30% fused alumina	Faint Tearing	Faint Tearing	Faint Tearing

(continued)

TABLE IV (concluded)

TEARING TESTS

Enamel	Initial Firing	First Reheat	Second Reheat
Chivit + 40% fused alumina	Faint Tearing	Faint Tearing	Tearing
Chivit + 10% silica	No Defects	Faint Hairlines	Very Faint Hairlines
Chivit + 20% silica	Severe Tearing	Severe Tearing	Severe Tearing
Chivit + 30% silica	Tearing	Faint Hairlines	Faint Hairlines
Chivit + 10% feldspar	Slight Tearing	Hairlines	Hairlines
Chivit + 20% feldspar	No Defects	Hairlines	Hairlines
Chivit + 30% feldspar	No Defects	Faint Hairlines	Faint Hairlines

TABLE V

MILL ADDITIONS VERSUS ADHERENCE

Mill Addition	Firing Temperature (° F)	Adherence Index
10% Calcined alumina	1525	99.0
20% Calcined alumina	1525	99.0
10% Fused alumina	1525	97.7
20% Fused alumina	1525	99.2
30% Fused alumina	1525	99.2
10% Silica	1425	98.9
20% Silica	1425	99.0
10% Feldspar	1500	99.6
20% Feldspar	1500	99.6
30% Feldspar	1525	99.6

29 The stretch test for adherence as described in Summary Report No. 1 is the only adherence test applicable for evaluating adherence of enamel to steel plate.

F. Welding Studies

30 An extensive welding study was undertaken in order to discover welding defects and their causes.

31 Up to the present time in our laboratory tests, welds have ordinarily been enameled more successfully than metal plate. In order to study possible defects in enamels on welds it was first necessary to have these defects show up in welding studies.

32 The first effort to produce a weld containing cavities was to try to produce a "cold" weld. A box was fabricated so as to spray water on the back side of a flat plate while a bead of weld metal was being deposited on the other side. The welding electrode used was AWS classification 6013. The welding generator was a Miller AC arc welder. Cold welds were made by using a combination of low current and cooling by spraying water on the back side of the plate being welded. These samples were coated with an enamel that would ordinarily fishscale on 3/16-inch steel plate. Fishscale appeared on the plate, but no fishscale appeared on the welds.

33 Hydrogen extraction tests were run on welds made in this manner. The hydrogen extracted seemed to be a function of the weld technique. The better the weld, the more hydrogen extracted. This could be due to the fact that occlusions in the weld form reservoirs and alleviate the hydrogen pressure.

34 The next attempt to form welds that would produce defects in enamels was to place materials that would form nonmetallic inclusions in the weld. The materials were placed between two plates of C1012 steel and AWS 6013 electrode used to butt weld the plates. Only a few scattered fishscales were formed in this manner on the weld. (See Table VI.)

35 The next attempt was to use a number of different AWS classification welding electrodes. (See Table VII.) The AWS electrodes that caused fishscale were as follows: 6016, 6027, 10013, and 10016. The 10016 electrode gave the worst fishscale directly on the weld. The 10013 class electrode gave fishscale on each edge of the weld. In this case the enamel came off the weld at the edge of the 1012 steel, leaving clean metal. Two plates were welded with AWS 10013 classification electrodes. One plate was enameled with an enamel very susceptible

TABLE VI

TENDENCY TO FISHSCALE VERSUS WELD ELECTRODE AND ENAMEL USED

Enamel	Mill Addition (Alumina)	6016	10013	10016
Pemco		Yes	No	No
Pemco	10% calcined	No	No	No
Pemco	20% calcined	No	No	No
Pemco	10% fused	No		No
Pemco	20% fused	No	Yes	Yes
Chivit		No	Yes	No
Chivit	10% calcined	No	No	No
Chivit	20% calcined	No	No	No
Chivit	10% fused	No		No
Chivit	20% fused	No		No
Chivit	30% fused	No		No
Chivit	40% fused	No		Yes
Ferro		Yes	Yes	No
Ferro	10% calcined	Yes		No
Ferro	20% calcined	No		No
Ferro	10% fused	Yes	No	No
Ferro	20% fused	No		No
O. Hommel		Yes		Yes
O. Hommel	10% calcined	No		No
O. Hommel	20% calcined	No		No
O. Hommel	10% fused	No	Yes	Yes
O. Hommel	20% fused	No		No

TABLE VII

WELDING ELECTRODE INFORMATION

AWS Classification	Current	Position	Coating	Remarks
E6013	AC or DC Straight and reverse	All	High titania or potassium	
E6016	AC or DC Reverse	All	Lime or lime titania	Low hydrogen
E6027	AC or DC Reverse	Horizontal and flat	Iron powder	
E10013	AC or DC Straight	All	Mineral	This electrode is usually used with chrome molybdenum steels
E10016	AC or DC Reverse	All	Lime or lime titania	Low hydrogen

to fishscale; the second plate was enameled with an enamel that does not ordinarily fishscale. The first plate fishscaled severely along the edge of the weld. The second plate had no fishscale whatsoever.

36 Welding electrodes from various manufacturers were evaluated. All electrodes of the same AWS class acted in the same manner when enameled, regardless of manufacturer.

37 Since earlier experiments showed that welds containing cavities were receptive to porcelain enamel, attempts were made to alleviate the gas pressure by drilling holes in the weld. Holes 1/16 inch in diameter were drilled in welds 3/4 inch apart. Two plates were coated with each enamel, one plate with holes and one without. In no case did the holes seem to make any difference.

G. Thermal Shock Tests

38 Thermal shock tests according to Mil-P-16961B, Paragraph 4.5.2.1 were run on 4-inch by 8-inch test plates, composed of two 4-inch by 4-inch by 3/16-inch steel plates joined by butt welding. One 4 by 4 was C1012 steel and the other was C1044. The plates were joined with AWS 10016 or AWS 6016 electrode. All plates were welded with a Miller AC arc welding generator. Samples were enameled with all enamels and with enamels containing mill additions of fused and calcined alumina. Four enamels passed five thermal shocks at each of the following temperatures: 650° F, 800° F, and 900° F, although some small fishscale appeared on each of these four enamels. The other enamels failed, with the largest percentage of failure being on the high carbon steel. A few plates failed because of defects in the enamel over the weld, but in most cases the weld had fewer defects than either plate.

39 In running thermal shock tests it was sometimes necessary to leave the plates overnight betweeen quenches. It was noted that fishscale developed on the plates during this period. The thermal shock test was then modified to allow only one quench from each temperature every 24 hours.

40 Enameled test plates used in the welding study, consisting of 6-inch by 4-inch by 3/16-inch C1012 metal with a bead of weld metal running down the center, were thermal shocked with only one quench being run every 24 hours. In this test the coating on the weld remained in much better condition than the coating on the C1012 metal.

41 Any enameled component subject to rapid cooling would probably not be cooled evenly on all sides. A thermal shock test that would rapidly cool an enameled piece on one side only would probably be of more value than the present test.

42 A spray box was constructed which enables cold water to be sprayed on one side of a 4-inch by 4-inch enameled plate. Two identical 4-inch by 8-inch plates were enameled for thermal shock testing. One plate was shocked by immersion in water. The second plate was placed on the spray box, and the plate sprayed with cold water on one side only. After four quenches, the enamel on the plate cooled on one side only had developed a very sandy feel. The plate shocked by immersion still had a glassy surface.

IV. FUTURE WORK

43 Four grades of steel ranging in carbon content from 0.05 to 0.50 per cent and in thickness of 3/16 and 1/4 inch have been ordered in sufficient quantity to insure a large number of tests for gas extraction, thermal shock, and observation of fishscale on enameled steel plates.

44 Efforts will be made to correlate the amount of gas extracted from a steel with its tendency to fishscale when samples are coated with one specific enamel and fired under the same conditions. The effect of mill additions of alumina on the above enamel will be investigated.

45 Efforts will be made to set the minimum amount of extractable gas from a steel when coated with a standard enamel in order for a steel not to have any delayed fishscaling defects.

46 Accelerated tests for fishscaling will be conducted by heating the enameled plates to 175° C for 48 hours and then raising the temperature five times in 50° C increments after each 48-hour period.

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

Respectfully submitted:

J. D. Walton
Project Director

J. N. Harris
Research Assistant

FINAL REPORT

PROJECT NO. A-308

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. N. HARRIS and J. D. WALTON

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CONTRACT NO. NObs 72209
INDEX NO. NS-061-087
BUREAU OF SHIPS CODE 312
DEPARTMENT OF THE NAVY

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

FEBRUARY 28, 1958

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

CODE SHEET

The following code is used throughout this report to designate manufacturers of materials used in this project.

Code	Manufacturer	Type
-A-	Chicago Vitreous Corp	Enamel
A-1	Chicago Vitreous Corp	Frit No. 259
A-2	Chicago Vitreous Corp	Frit No. 289
-B-	Ferro Corporation	Enamel
-D-	Pemco Corporation	Enamel
-S-	O. Hommel Company	Enamel†
S-1	O. Hommel Company	Frit No. 230
S-2	O. Hommel Company	Frit No. 231
S-3	O. Hommel Company	Frit No. 232
-V-	J. M. Tull Co.	Cold Finished 1018 Steel
-W-	U. S. Steel	
-X-	Inland Steel	
-Y-	Atlantic Steel	
-Z-	J. T. Ryerson	
-1-	O. Hommel Company	Clay No. 540
1-a, 1-c	O. Hommel Company	Clay No. 540††
1-b	O. Hommel Company	Clay No. 540†††

† This enamel is used as the Standard Enamel.

†† As supplied to the Warren Company of Atlanta.

††† Purchased by Georgia Tech from O. Hommel.

(Continued)

CODE SHEET (Continued)

Code	Manufacturer	Type
-2-	Ferro Corporation	Green Label Clay
-3-	Ferro Corporation	Red Label Clay
-4-	Ferro Corporation	Black Label Clay

MANUFACTURERS OF REQUIRED MATERIALS

Vendors	
G	Scientific Glass Apparatus Co., 105 Lakewood Terrace, Bloomfield, New Jersey.
H	Will Corporation New York 12, New York (Catalog 6)
J	Arthur H. Thomas Co. Philadelphia, Pennsylvania (1950 Catalog)
K	Corning Glass Works, Corning, New York
E	Precision Scientific Co., Chicago, Illinois
F	Central Scientific Co., Chicago, Illinois

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

FINAL REPORT

PROJECT NO. A-308

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. N. HARRIS and J. D. WALTON

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

FEBRUARY 28, 1958

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I. ABSTRACT

This project was initiated as Project No. A-308, Contract No. NObs 72209 as a continuation of Project No. A-204, Contract No. NObs 66521 and covers the period of work from November 1956 to February 1958. The title of both projects was "Porcelain Enameling Quality Steel Plates and Weldments."

From this work a possible procedure was set up for qualifying steel plate acceptably receptive to porcelain enamel by the use of a "standard enamel." Final testing showed a definite relationship between gas extracted and alumina content of the enamel but no definite relation between the type of steel and enamel defects. The scope of the work performed is indicated.

Enameling materials obtained for testing were four new low temperature ground coat enamels, and various grades of steel in 3/16 and 5/8 inch thickness.

Tests were run to determine the effects of type of enameling clay used, mill additions, firing atmosphere, firing temperature and length of firing time. Tests devised for this study were:

(1) Gas† extraction

(2) Thermal shock

(3) Tearing and hairlining

(4) Adherence

(5) Oxidation of steel

(6) Wettability of steel

A welding study was also initiated to study defects of enamels on welds by the use of a number of different electrodes of AWS classification and by

†B. J. Sweo, "Gases in Enameling," J. Can. Ceram. Soc. 25, 39 - 46 (1956)

the use of a series of welding techniques designed to produce welds that cause defects. The above listed tests were used in qualifying the enameled welds.

Project Report No. 1 describing the construction and operation of the gas extraction apparatus is included as an appendix.

II. PURPOSE

This project was initiated on October 31, 1956, with the following objectives:

(1) The development of a complete and technically accurate description of steel plates and welds of steel plates acceptably receptive to porcelain enamel coatings. This description was to be incorporated into material specifications for government procurement.

(2) The determination of the factors which affect the enameling characteristics of steel plates and welds.

(3) The establishment of the validity of parameters.

(4) The establishment of the limits of quality control for enamelability of steel plates and welds.

(5) The assessment of the factors responsible for defective coated parts intended to conform to Specifications Mil-P-16961.

III. EXPERIMENTAL WORK

A. Introduction

In order to carry out the objectives of Contract NObs 72209, which is a continuation of the work begun under NObs 66521, the following line of experimental work was undertaken.

Low temperature porcelain enamel ground coat frits were secured from four different manufacturers. Steel plates of various carbon contents were acquired in sufficient quantities for fabricating T-joint specimens. In order to continue and facilitate the study of the manifestations of gas in steel, additional units of the gas extraction apparatus developed under Contract NObs 66521 were fabricated.

A program was also undertaken to study the effect of (1) the oxidation characteristics of steel and (2) wettability of steel in the presence and absence of oxygen, as related to (a) enamel adherence, (b) thermal shock resistance and (c) tendency to fishscale. Thermal shock tests were performed on T-sections according to the schedule of Mil-P-16961B.

New tearing and thermal shock tests were devised to expand on the defects shown by the T-joint test.

A welding study was initiated to study defects in enamel coatings on welds.

B. Enamel Variables

In order to pass the thermal shock test of Mil-P-16961B, the following work was done.

1. Frit Evaluation

Since alumina additions to enamels improve their thermal shock resistance but require higher firing temperatures, it was decided that newly developed low temperature ground coat frits would be used in this phase of the project. Thus, maximum alumina could be added before firing temperatures generally used in industry would be exceeded. Low temperature porcelain enamel ground coat frits were secured from four manufacturers: -A-, -B-, -D-, -S-.

The following mill addition was selected for all preliminary testing.

100 parts frit†

6 parts Clay No. -1-

4 parts silica

1/2 part borax

1/8 part bentonite

1/8 part magnesium carbonate

50 parts water

All frits were milled with this mill addition to a fineness of 6 to 8 grams of a 50-ml sample of slip retained on a 200-mesh screen after washing and drying.

Since the most difficulty in obtaining good enamel coatings on T-joint specimens under Contract NObs 66521 was with the 3/16-inch metal, it was decided to use only 3/16-inch metal sections during preliminary testing. Three-sixteenth-inch steel plate which produced fishscale when enameled in a moist atmosphere with the "conventional" enamels used under Contract Nobs 66521 was selected for coating. Samples, 4- by 8- by 3/16-inch, were coated by spraying and fired at 1350° F in dry and wet atmospheres. In no instances were any fishscale produced even when the moisture content of the furnace atmosphere was raised to 100 ml of water per cubic foot of furnace volume. The optimum

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†This mill batch becomes the basis for "Standard Enamel" when the frit formulation on page 37 is used.

temperature was established by microscopic examination of the bubble structure and by testing adherence on 20-gage enameling iron. The adherence test consisted of dropping a known weight a certain distance and indenting a 20-gage section of enameled metal. The amount of enamel chipped off the metal was measured by a Porcelain Enamel Institute adherence meter. Samples giving the highest adherence index were selected as representing the proper firing temperature.

In order to confirm the fishscale producing property of this steel, it was coated with the enamel used under Contract NObs 66521 in both normal and wet (100 ml/cu ft) atmospheres. Both conditions produced fishscale. With the wet atmosphere, the surface of the enameled plate was covered with fishscale, the greatest distance between any two fishscales being no greater than 1/8 inch.

Large quantitites of each frit were obtained originally but these were exhausted and new supplies of both frit and clay had to be obtained. Metal sprayed with the new batches of enamel fishscaled severely almost immediately upon cooling. Mill additions of alumina sufficient to give the enamel a 10-per-cent-alumina content caused a lessening of fishscale but did not completely stop it. Enamel containing 20 per cent of alumina stopped fishscaling. Investigations to determine the cause of enamel defects in the new batch of materials showed the enamel structure to be different from that of the old batch.

C1012 steel plates, 4- by 4- by 3/16-inch, were sprayed with the original and new batches of enamel made from the frits obtained from manufacturers -A-, -B-, and -S-. Three plates, one for each source, were sprayed with the original enamel, and three plates, one for each source, were sprayed with the new enamel. The six plates were fired at the same time in the inconel chamber (Figure 1) with a wet atmosphere for 22 minutes at 1375° F. All new batches of the three enamels fishscaled severely on cooling. The original enamel from manufacturer -B- developed a few shiner scale and the enamels from manufacturers -A- and -S- failed to develop fishscale. Investigations of the enamels under the microscope showed the bubble structure of the original enamels to be much larger than the bubble structure of the new batch of enamels.

In the case of the enamel from manufacturer -S- the frits used for the new batch of enamel were taken from the original supply of frits. For the enamels from manufacturers -A- and -S- the new supply of frits had to be used. For all three enamels it was necessary to use Clay No. 1-b.

For the six test plates fired in the inconel chamber, fineness of all enamels was 6 to 8 grams and specific gravity was 1.7. All coatings applied to the 3/16-inch plates were the same thickness. The six 3/16-inch plates were cut from the same strip of AISI C1012, and were fired together for the same length of time.

Figures 2, 3, 4, 5, 6 and 7 show the difference in bubble structure between original and new batches of the three enamels.

The original supply of Clay No. -1- was obtained as a 5-pound sample from a local enameling company (1-a). The new supply of No. -1- Clay was ordered directly from the manufacturer (1-b). In order to be certain that the original sample obtained from the enameling company was Clay No. -1-, another sample was obtained at a later date from their supply of No. -1- clay and was designated 1-c . Two identical one-gallon mills were made up

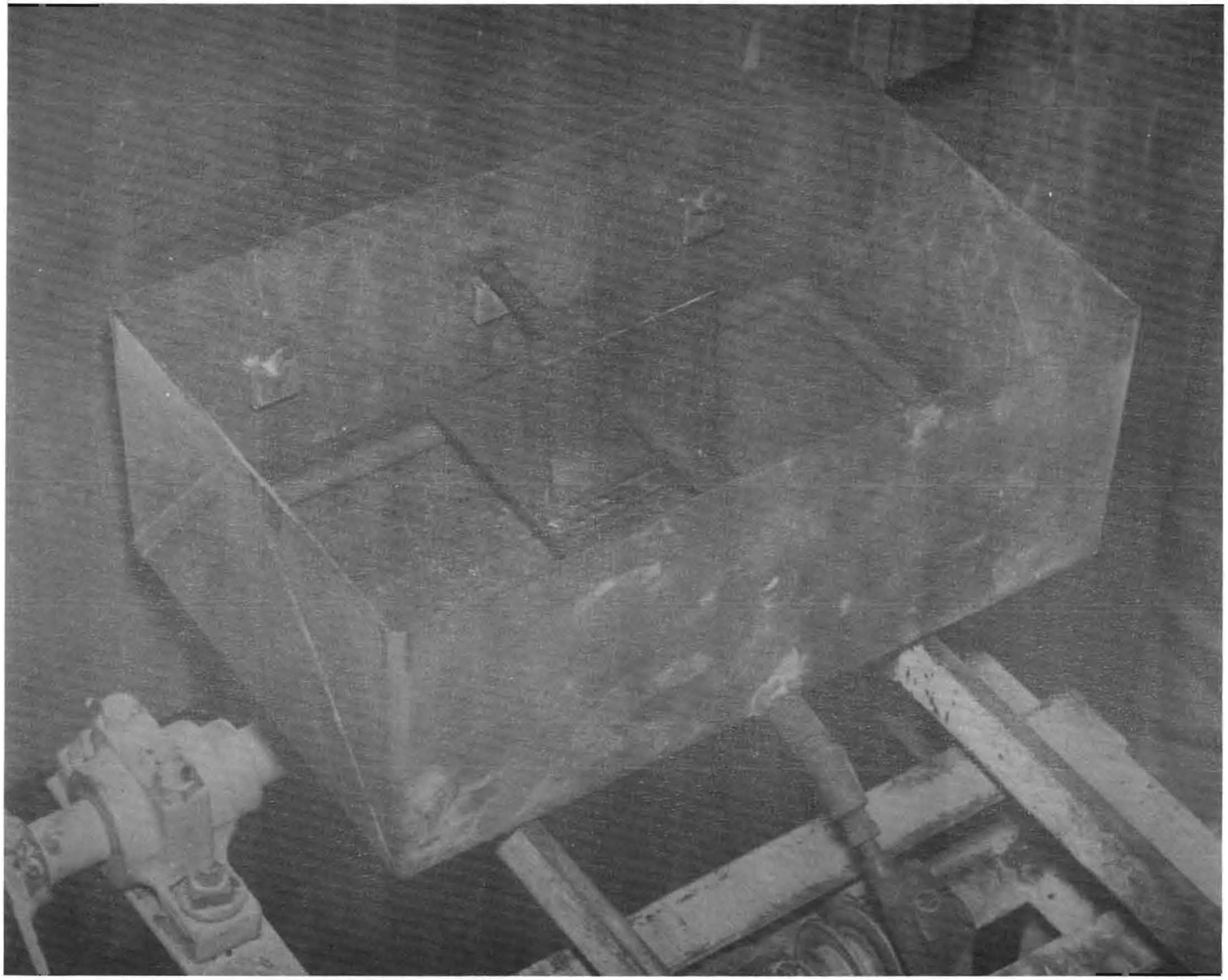

Figure 1. Firing Chamber for Controlled Atmosphere Firing.

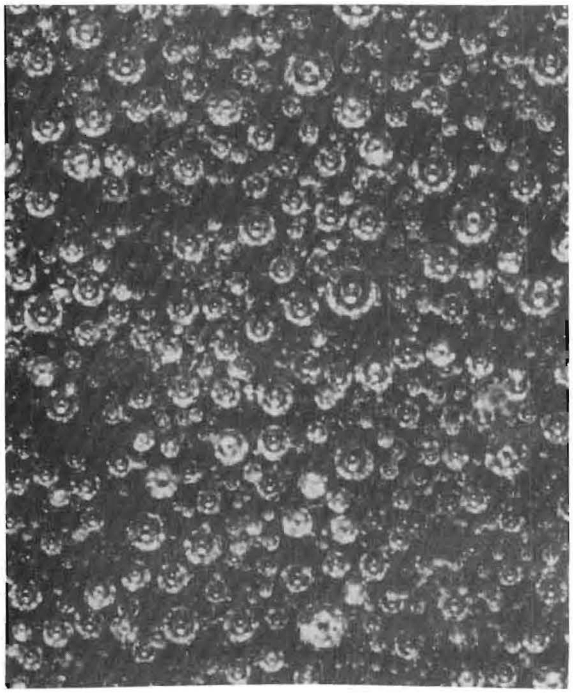

Figure 2. Bubble Film of -A- Enamel Using Clay No. 1-a (60X).

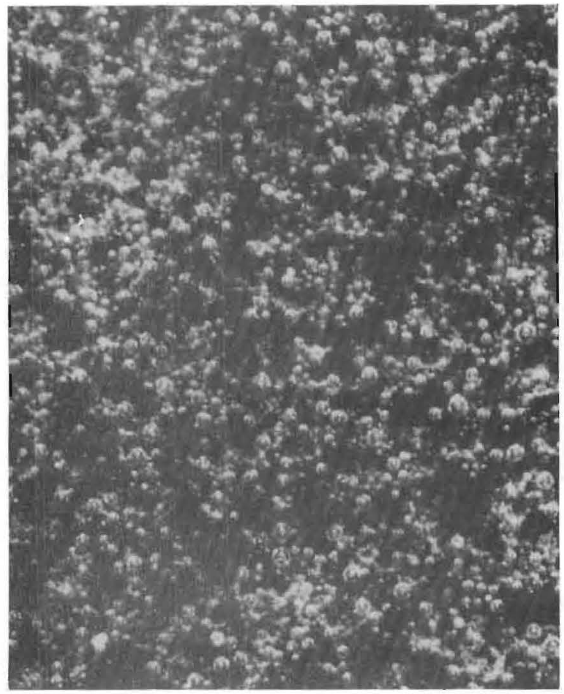

Figure 3. Bubble Film of -A- Enamel Using Clay No. 1-b (60X).

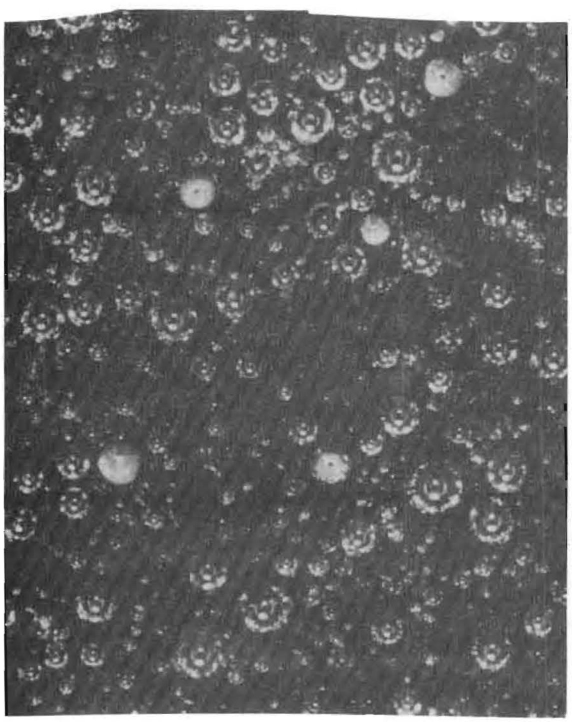

Figure 4. Bubble Film of -B- Enamel Using Clay No. 1-a (60X)

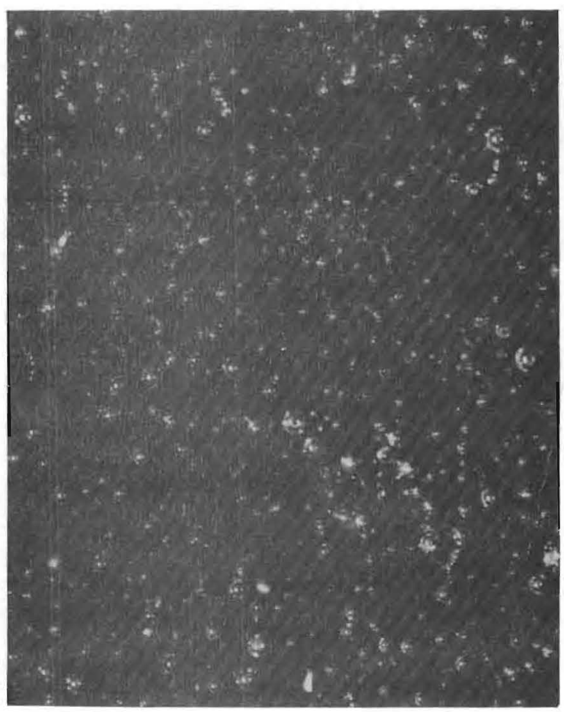

Figure 5. Bubble Film of -B- Enamel Using Clay No. 1-b (60X).

using the enamel formulation in Section B. One mill was made with the clay from the enameling company and the other mill was made with the clay obtained directly from the manufacturer. Two 4- by 8- by 3/16-inch samples cut from the same metal were sprayed and were fired at the same time. Figure 8 shows the bubble structure of the enamel made with the clay obtained from the enameling company and Figure 9 shows the enamel containing the clay obtained directly from the manufacturer. The enamel in Figure 8 did not fishscale but the enamel in Figure 9 developed a number of shiner scales.

At a later date, a reorder for manufacturer -A's- Frit No. A-1 was placed. It was found that this frit had become obsolete and had been replaced by No. A-2. The enamels made with the A-2 frit gave a brown coating and developed a bubble structure containing smaller bubbles than the enamel made with the A-1 frit. This led to the belief that procurement of frit and clay by brand and number is not reliable.

2. Bubble Structure

The size of the bubbles in the bubble stratum would seem to be an important factor as to whether an enameled plate will fishscale. Three enamels were made with -S- frits, substituting Clays -2-, -3-, and -4-, for Clay No. -1-. These enamels were sprayed on 3/16-inch C1012 steel plates and fired in a wet atmosphere. The plates coated with the enamel made with Clay No. -2- had large, well-spaced bubbles in the bubble stratum, and as expected, very few fishscales. The enamels containing Clay No. -3- had smaller bubbles than the previous plates and had more fishscale. The enamel made with Clay No. -4- had very small bubbles and fishscaled severely.

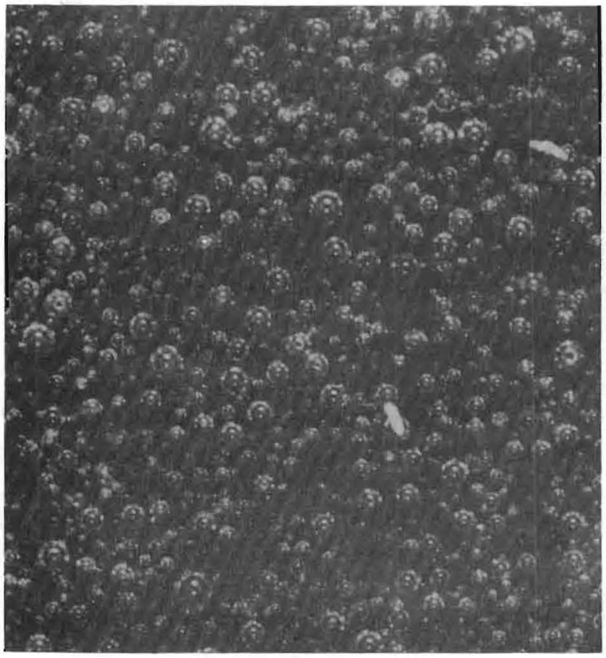

Figure 6. Bubble Film of -S- Enamel Using Clay No. 1-a (60X).

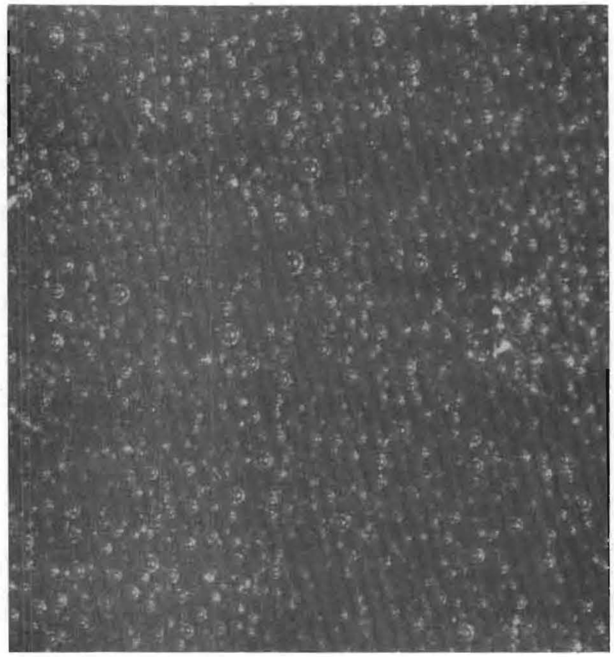

Figure 7. Bubble Film of -S- Enamel Using Clay No. 1-b (60X).

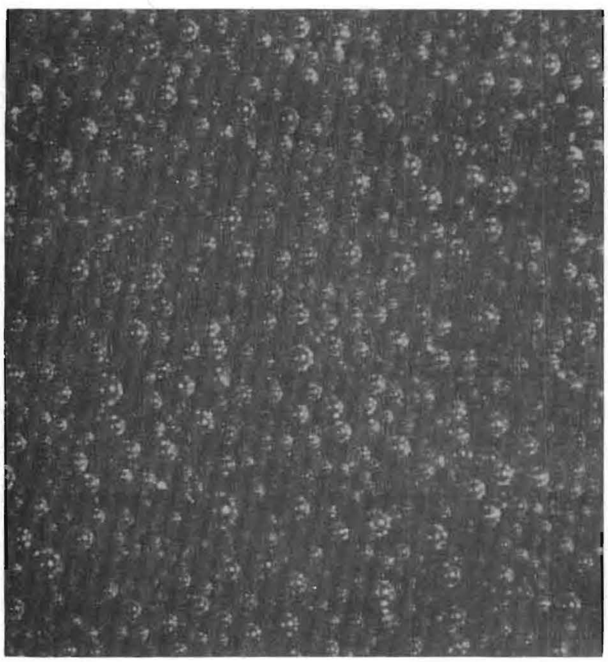

Figure 8. Bubble Film of -S- Enamel Using Clay No. 1-c Fired in a Smaller Furnace. (60X).

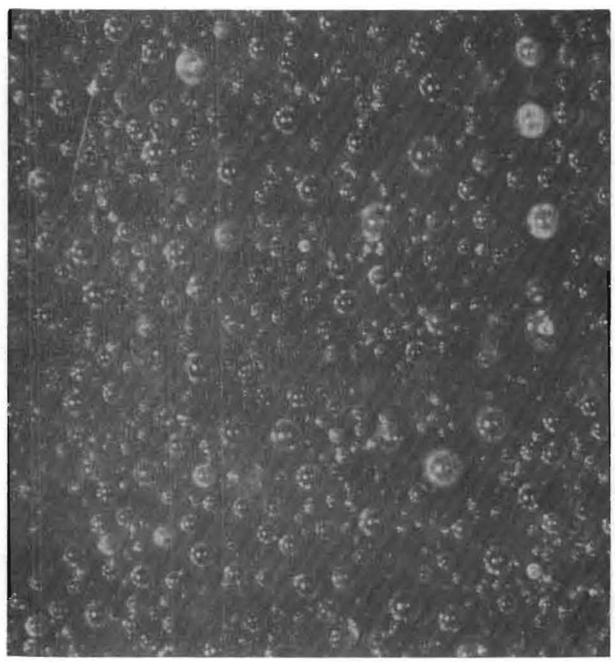

Figure 9. Bubble Film of -S- Enamel Using Clay No. 1-b Fired with Sample of Figure 8. (60X).

3. Mill Addition Studies

Studies were made of the effects of various mill additions as related to fishscale and adherence of enamels. In all studies the mill batch formulation mentioned previously in this report was used. All mill additions were either additions to, or variations of, this formula.

The clay content of an enamel was varied from one to nine parts clay, keeping all other components the same. Fishscaling decreased gradually and bubble size increased up to six parts clay. Above six parts clay, fishscaling continued to decrease; however, bubble spacing increased up to abnormally wide separation, and the bubble structure began to have the appearance of one to which additions of alumina had been made.

Mill addition studies were made by varying the silica content from 0 to 30 parts silica. Less than four parts silica gave an acceptable bubble structure if fired at the proper temperature; however, the firing range was very narrow. Ten parts silica gave a fairly well developed bubble structure, a much wider firing range, and very little fishscale. Twenty parts gave no fishscale but had very few and very fine bubbles in the bubble structure. Further pursuit of the silica variation study was discontinued because the enamels thus produced were of poor fit and therefore believed to have poor resistance to thermal shock.

Mill additions of potassium feldspar were also made but the only effect of additions of 10, 20 and 30 parts was to make the enamel more refractory.

Mill additions of 10, 20 and 30 parts of pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$) were tried but blistering and bubbling of the coating caused this work to be discontinued.

C. Thermal Shock Tests

Each of the enamels from the four companies was milled with 20 per cent of calcined unground alumina. A 4- by 8- by 3/16-inch plate of C1012 steel was coated with each enamel with and without the alumina. The firing schedule of the alumina-free enamel was 1325° F for 17 minutes and 1400° F for 17 minutes for the enamels with 20 per cent of alumina. All plates were subjected to the thermal shock schedule of Mil-P-16961B, including the five quenches from 900° F. The plates coated with the 20-per-cent-alumina enamels showed no effect from the thermal shock treatment, even on the edges of the plate. These enamels had a very satiny finish due to the alumina addition and kept this finish throughout the thermal shock treatment. The plates coated with the alumina-free enamel passed the thermal shock test; however, the surface which was very smooth and glassy prior to shocking was sandy to the touch and had a "frosty" appearance after the thermal shock treatment.

No evidence of fishscaling was apparent since test plates had been coated with enamels made with Clay No. 1-a. Enamels made from 1-b showed some evidence of fishscaling after thermal shocking. The degree of fishscaling was to some extent dependent on the enamel used.

T-joint specimens were fabricated from AISI C1012 steel which was secured in the form of 4- by 3/16-inch strips and 4- by 5/8-inch flats.

The component pieces were welded and assembled according to the methods used in Contract No. NObs 66521 except that welding was accomplished by the manual arc method utilizing a d-c welding generator using reverse polarity.

Cleaning was accomplished by sandblasting and enamel was applied by dipping. Firing was on an open rack in the furnace with a normal air atmosphere. Firing temperature was 1475° F for enamels containing 10 per cent of alumina and 1425° F for the enamel from manufacturer -D- containing 7-1/2 per cent of alumina. Thermal shock tests were conducted on the T-sections according to the schedule of Mil-P-16961B. Tests were conducted with enamels from manufacturers -A-, -B-, and -S- containing 10-per-cent additions of alumina. The enamel from manufacturer -D- had a 7-1/2-per-cent addition of alumina. Enamels from all four companies passed the 900° F shock test. Initially, larger additions of alumina were added to the enamels but draining and firing problems caused a re-evaluation of the advantages of high alumina content.

Thermal shock tests according to Mil-P-16961B, Paragraph 4.5.2.1, were run on 4- by 8-inch test plates composed of two 4- by 4- by 3/16-inch steel plates joined by butt welding. One 4 by 4 was C1012 steel and the other was C1044. The plates were joined with AWS 10016 or AWS 6016 electrodes. All plates were welded with an a-c arc welding generator. Samples were enameled with all enamels and with enamels containing mill additions of fused and calcined alumina. Four enamels passed five thermal shocks at each of the following temperatures: 650° F, 800° F, 900° F, although some small fish-scale appeared on each of these four enamels. The other enamels failed, with the largest percentage of failure being on the high carbon steel. A few plates failed because of defects in the enamel over the weld, but in most cases the weld had fewer defects than either plate.

In running thermal shock tests it was sometimes necessary to leave the plates overnight between quenches. It was noted that fishscale developed on the plates during this period. The thermal shock test was then modified to allow only one quench from each temperature every 24 hours.

Enameled test plates used in the welding study, consisting of 6- by 4- by 3/16-inch C1012 metal with a bead of weld metal running down the center, were thermal shocked with only one quench being run every 24 hours. In this test the coating on the weld remained in much better condition than the coating on the C1012 metal.

Any enameled components subject to rapid cooling would probably not be cooled evenly on all sides. A thermal shock test that would rapidly cool an enameled piece on one side only is of more value than the test in which the enamel is cooled on both sides.

A spray box was constructed which enables cold water to be sprayed on one side of a 4- by 4-inch section of an enameled plate. Two identical 4- by 8-inch plates were enameled for thermal shock testing. One plate was shocked by immersion in water. The second plate was placed on the spray box, and the plate sprayed with cold water on one side only. After four quenches, the enamel on the plate cooled on one side only had developed a very sandy feel. The plate shocked by immersion still had a glassy surface (Figure 10.).

D. Tearing Studies

As a supplement to the enamel defects shown up by T-joint sections and to determine tearing and hairlining properties of enamels, the following test was used. The test plate was composed of two pieces of 14-gage enameling quality, low-metalloid steel that were spot welded together. (See Figure 11) The front plate was 5-1/2 by 8 inches, and the back plate was 2-1/4 by 5-1/2 inches. The test plates were pickled and nickel flashed. Slip consistency of enamels

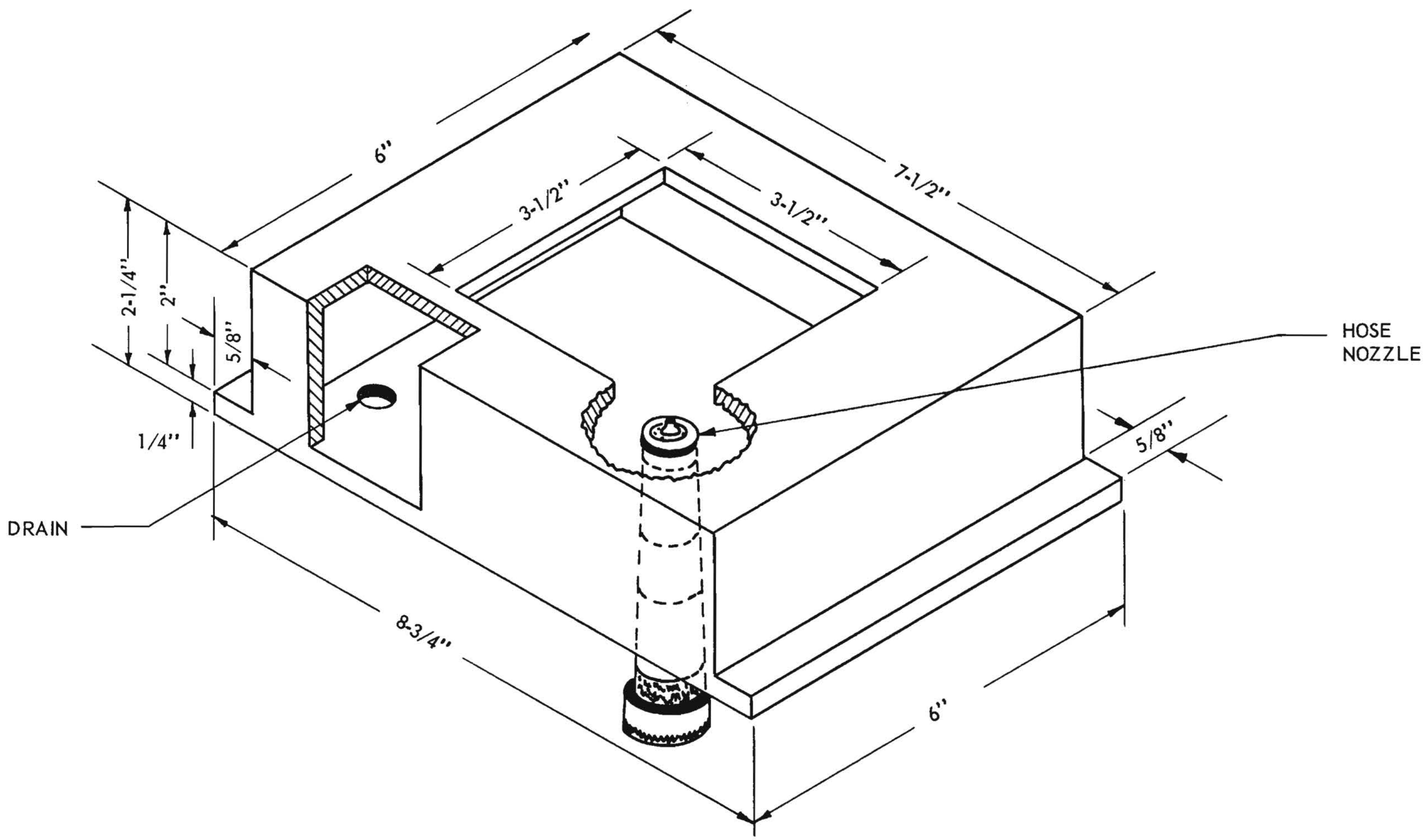

Figure 10. Line Drawing of Spray Box

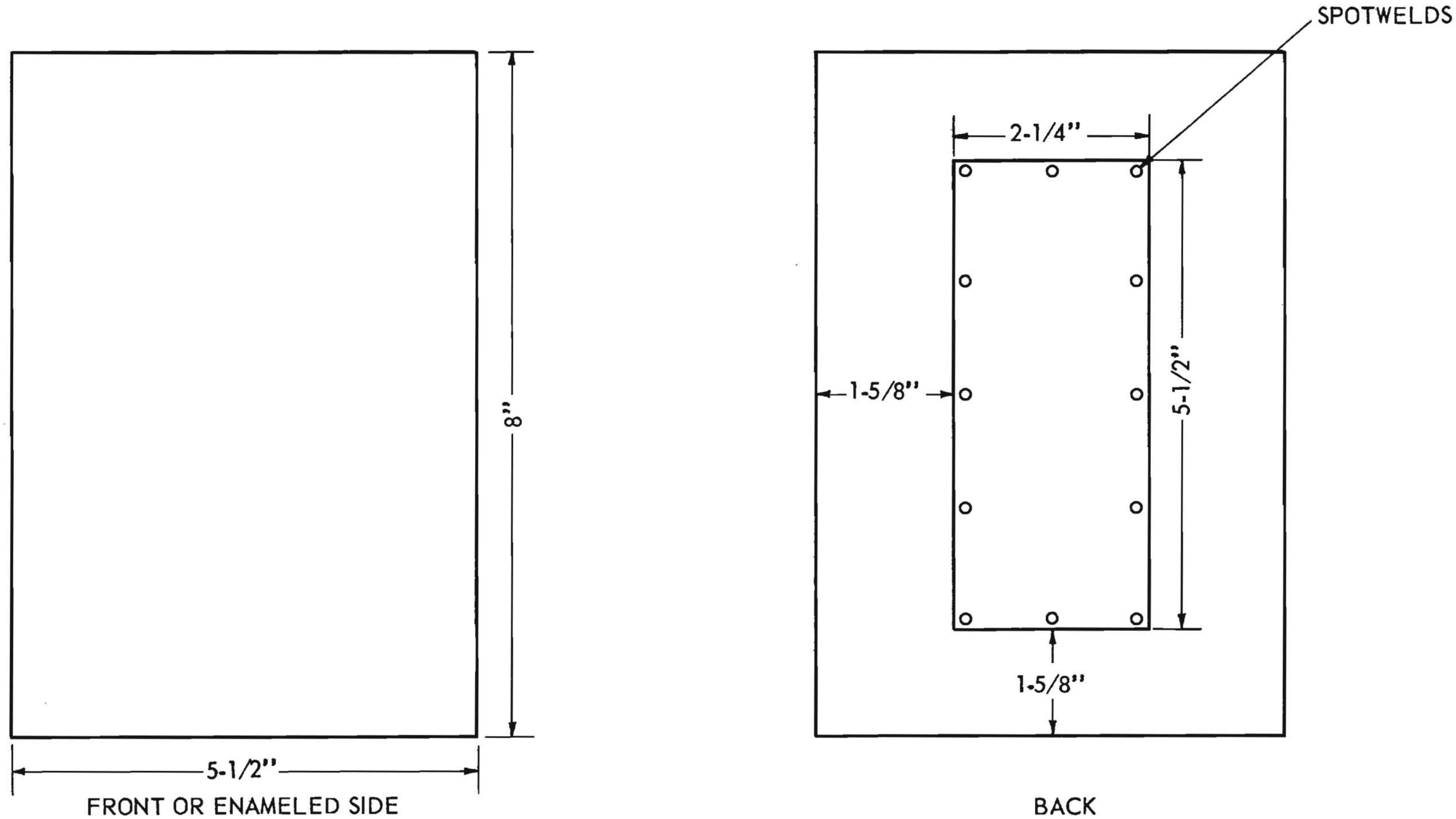

Figure 11. Construction of Tearing Test Sheets.

tested was controlled by carefully weighing all ingredients according to the batch formula listed in Section B of this Chapter and grinding to a fineness of 6 to 8 grams retained on a 200-mesh screen when a 50-ml sample of slip was poured and washed through the screen. The specific gravity was adjusted to 1.7 by the addition of water. The ground coat enamel to be tested was then sprayed on the front of the test plate, dried and fired for 5 minutes at the optimum temperature for the enamel being used. The plate was allowed to cool, observed for tearing and then reheated to 1000° F for 10 minutes. The plate was allowed to cool, observed for hairlining and again reheated to 1000° F for 10 minutes. After cooling, observations were again made for hairlining. Table I shows the results of this test. It can be seen from the table that the best results were obtained with the enamels containing 10 and 20 per cent of fused alumina. The enamels containing 10 per cent of calcined alumina gave good results, but a problem of tearing developed at higher percentages (Figure 11). Tearing had previously occurred when these enamels were applied to T-sections. Fused alumina is preferred over calcined alumina for this reason. Enamels containing only normal mill additions developed hairlines upon reheating (Figure 11). This possibly explains the reason that these enamels develop a "sandy feel" during thermal shock testing. The silica and feldspar additions had little effect on the tearing and hairlining properties of enamels. The effects of the tearing tests on each enamel are shown in Table I.

E. Adherence

Adherence tests were run according to the method of J. E. Sams described in "Proceedings of the Fifth Annual Forum," Porcelain Enamel Institute, 1940.

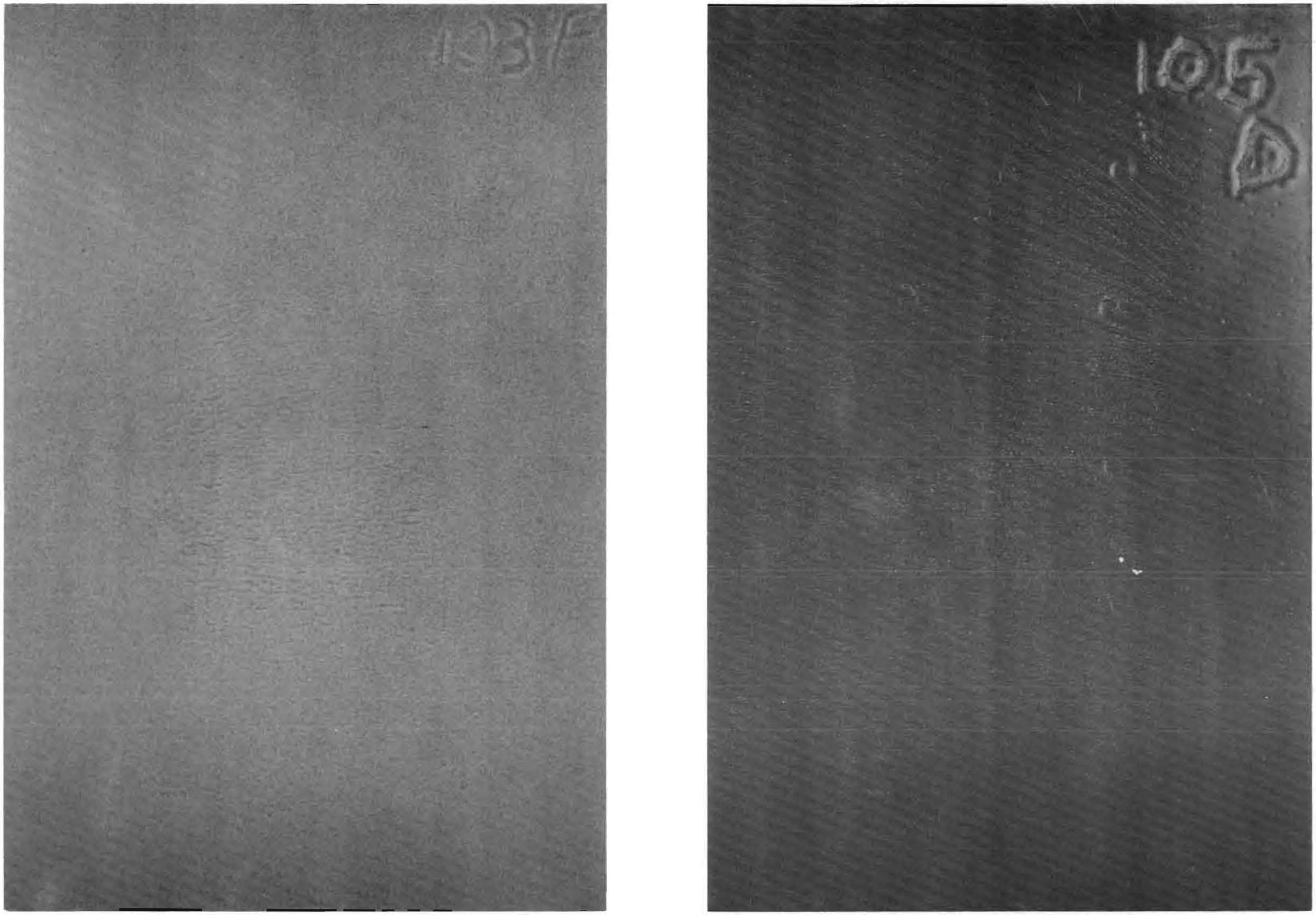

Figure 12. Tearing Test Sheets Showing Tearing and Hairlining.

TABLE I

TEARING TESTS

Enamel	Initial Firing	First Reheat	Second Reheat
-D-	No defects	Hairlines	Hairlines
-D- + 10% calcined alumina	No defects	Hairlines	Faint hairlines
-D- + 20% calcined alumina	Bad tearing	Bad tearing	Bad tearing
-D- + 10% fused alumina	No defects	Faint hairlines	Faint hairlines
-D- + 20% fused alumina	No defects	No defects	Very faint hairlines
-B-	No defects	Very faint hairlines	Very faint hairlines
-B- + 10% calcined alumina	No defects	Hairlines	Hairlines
-B- + 20% calcined alumina	Bad tearing	Some healing	No change
-B- + 10% fused alumina	Faint tearing	Hairlines	Hairlines
-B- + 20% fused alumina	Change in color	Faint hairlines	Faint hairlines
-S-	No defects	Hairlines	Hairlines and slight tearing
-S- + 10% calcined alumina	Slight tearing	Slight tearing	Slight tearing
-S- + 20% calcined alumina	Bad tearing	Some healing	No change
-S- + 10% fused alumina	Slight tearing	Hairlines	Hairlines
-S- + 20% fused alumina	Slight tearing	Faint hairlines	Faint hairlines

(Continued)

TABLE I (Concluded)

TEARING TESTS

Enamel	Initial Firing	First Reheat	Second Reheat
-A-	No defects	Hairlines	Hairlines
-A- + 10% calcined alumina	Slight tearing	Tearing and hairlines	Tearing and hairlines
-A- + 20% calcined alumina	Bad tearing	Some healing	No change
-A- + 10% fused alumina	Faint tearing	Faint tearing	Faint tearing
-A- + 20% fused alumina	No defects	No defects	No defects
-A- + 30% fused alumina	Faint tearing	Faint tearing	Faint tearing
-A- + 40% fused alumina	Faint tearing	Faint tearing	Tearing
-A- + 10% silica	No defects	Faint hairlines	Very faint hairlines
-A- + 20% silica	Severe tearing	Severe tearing	Severe tearing
-A- + 30% silica	Tearing	Faint hairlines	Faint hairlines
-A- + 10% feldspar	Slight tearing	Hairlines	Hairlines
-A- + 20% feldspar	No defects	Hairlines	Hairlines
-A- + 30% feldspar	No defects	Faint hairlines	Faint hairlines

The sample size selected for use in this test was 2 by 9 by 3/16 inches. After sandblasting, the specimen was ground coated by spraying and then dried. Before firing, 3 inches of enamel were brushed from each end, leaving a 3-inch strip in the center undisturbed.

After firing, an extensiometer which was constructed for this test was attached to the specimen on each side of the enamel strip. The entire assembly was then set up in a 60,000-lb tensile test machine.

Stretching of the piece was begun and was continued until the extensiometer indicated 6-per-cent elongation of the desired 3-inch test area in the center. Stretching was at the rate of 0.5 inches per minute. Figure 13 shows the apparatus for stretch testing adherence of enamel to steel plate.

Adherence count was determined by means of a PEI adherence meter. (See Figure 14.) The meter essentially consists of 169 electrical probes. Each probe registers one count when bare metal is contacted. The probe circle has three positions and three cycles are run, giving a count of 507. Maximum adherence is measured by a count of zero. Figure 15 shows curves on adherence studies of a C1012 steel. With the -A-, -B- and -D- enamels maximum adherence was obtained with a 10-per-cent addition of alumina, but with the -S-, maximum adherence was obtained with a 20-per-cent addition of alumina. This difference in adherence cannot be accounted for at this time.

Table II gives average adherence count versus carbon content for all steels tested. Reproducibility of results with the lower carbon steel was very difficult because of the Luder's lines which follow lines of strain. These lines become less evident in the higher carbon ranges. Figure 16 is of steels

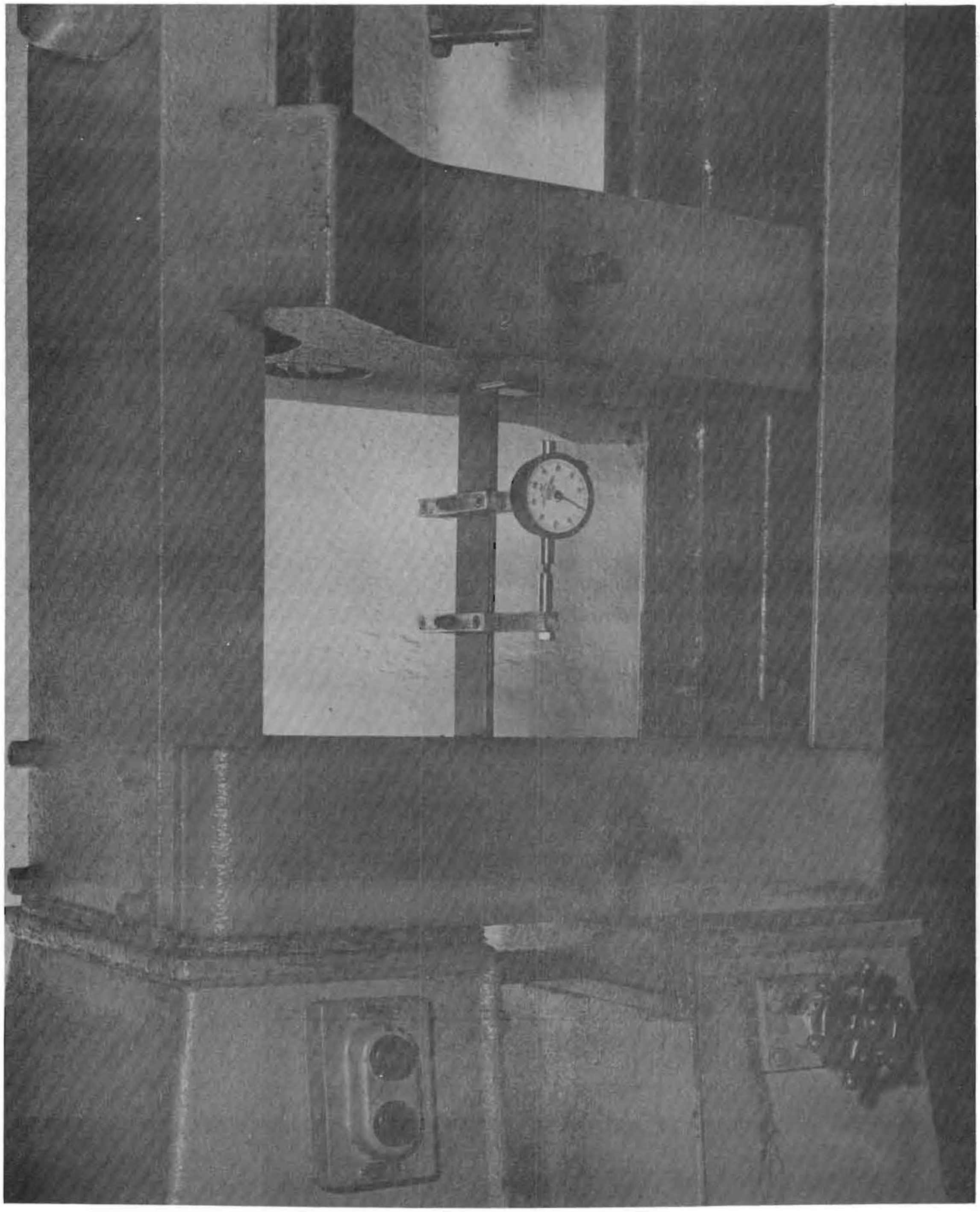

Figure 13. Apparatus for Stretch Testing Adherence of Enamel to Steel Plate.

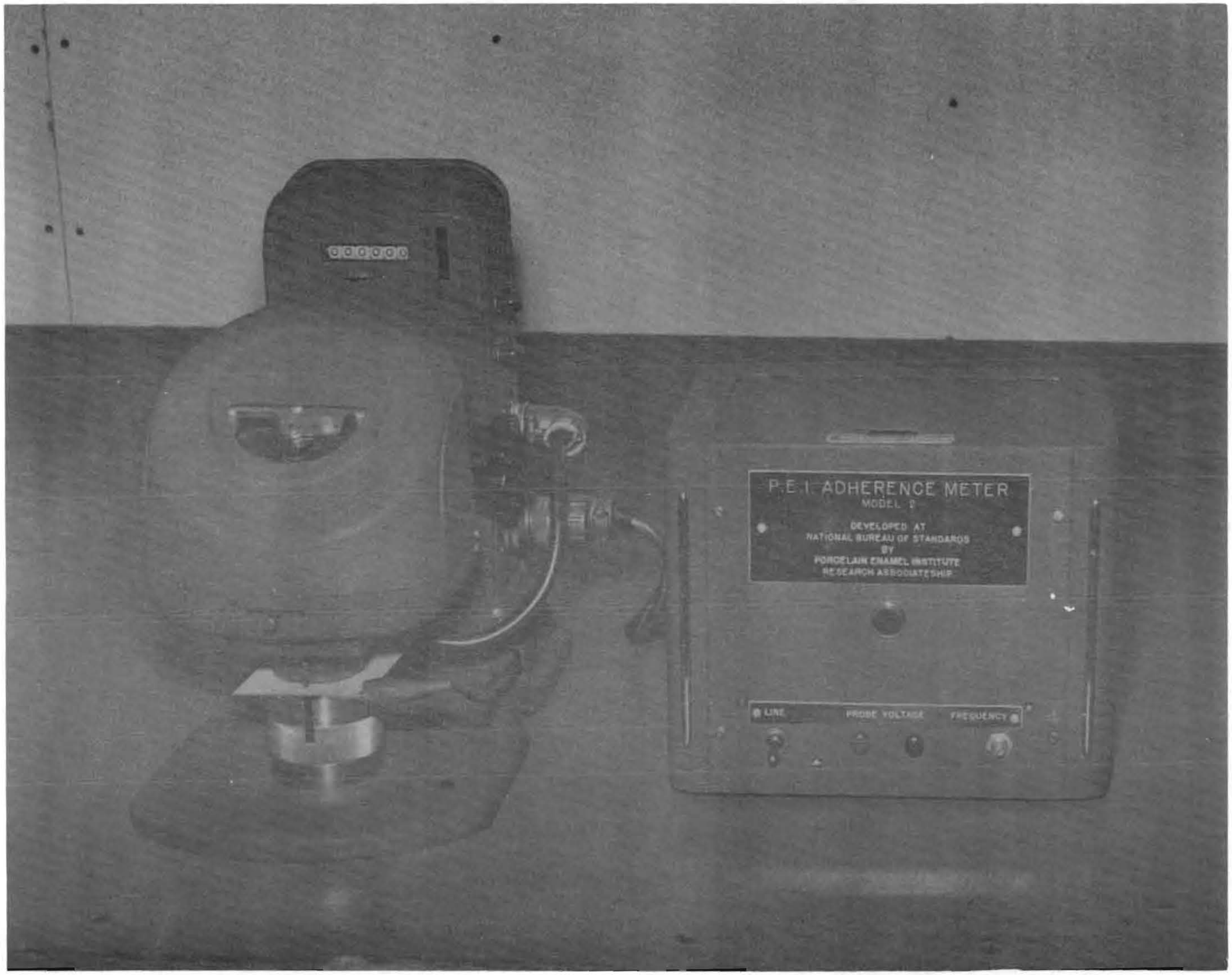

Figure 14. PEI Adherence Meter.

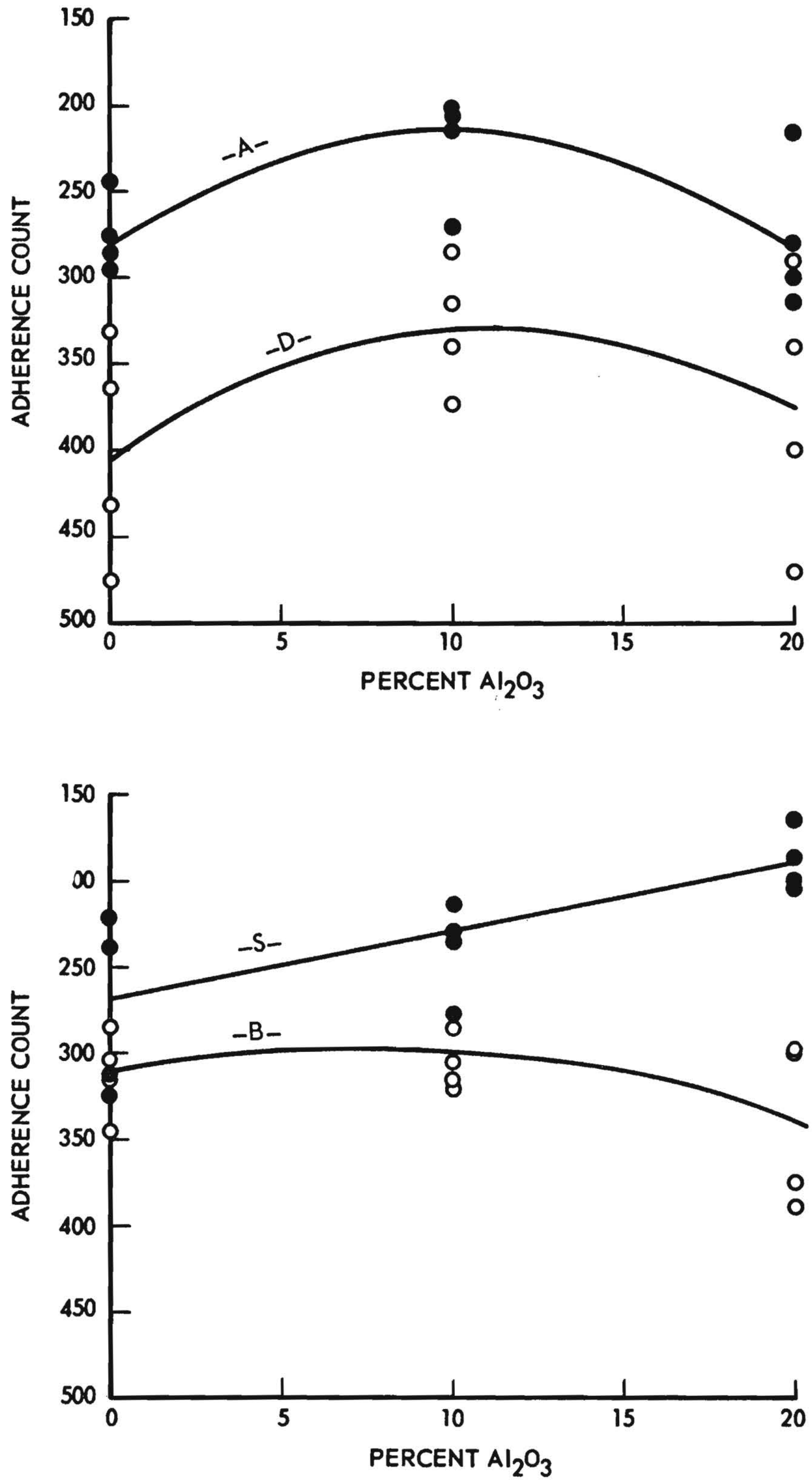

Figure 15. Per Cent Alumina Versus Adherence Count.

Figure 16. Low and High Carbon Steels After Stretching, Showing Effect of Luder's Lines.

of carbon content 0.04 and 0.36 per cent. The Luder's lines can be seen very clearly in the low carbon steel.

TABLE II

AVERAGE ADHERENCE OF ENAMEL VERSUS CARBON CONTENT OF STEEL

	Average Adherence of Enamel				
Enamel	0.04% Carbon	0.12% Carbon	0.19% Carbon	0.27% Carbon	0.36% Carbon
-D-	381†	405	316	473	455
-D- + 10% calcined alumina	463	345	488	463	488
-A-	250	275	250	190	209
-A- + 10% calcined alumina	301	225	212	194	215
-B-	299	305	372	295	284
-B- + 10% Calcined alumina	321	305	287	268	244
-S-	350	260	318	212	302
-S- + 10% calcined alumina	231	245	223	211	199

†507 = no adherence,
0 = perfect adherence.

F. Steel Evaluation

1. Oxidation Studies

In order to evaluate the effect of metal oxidation on enamel defects, a series of oxidation tests were run on a number of samples of steel of varying carbon content.

Preliminary tests were run to standardize a procedure so that results would be reproducible. A representative number of 2- by 2-inch samples of C1012 steel were sandblasted and cleaned with alcohol. The samples were placed on wire racks at various spots in the inconel chamber used for gas extraction (Figure 1). Dry air was pumped into the chamber at a rate of 8 liters per minute for 10 minutes before placing the chamber in the furnace at 1400° F for 20 minutes. The air was allowed to run throughout the heating and cooling cycle. The chamber was cooled to room temperature before removing samples from it. Samples were then reweighed to determine the weight of oxide. Tests were run with dry air, moist air and carbon dioxide. All results obtained were reproducible within 5 per cent.

Five steels with carbon contents of 0.04, 0.12, 0.19, 0.27 and 0.36 per cent were selected for oxidation studies. Two samples of each steel were sandblasted, cleaned, weighed, fired and reweighed to determine the amount of oxide. The procedure used was the same as that used in determining the reproducibility of results. Tests were run with wet and dry atmospheres of air and with an atmosphere of carbon dioxide. Figure 17 and Table III show the results of these oxidation studies. Oxidation decreases as carbon content increases. Also, limits of reproducibility tend to improve with increase in carbon content.

2. Wettability Studies

In order to determine the effect of oxidation of steel on the ability of an enamel to wet the steel, the following test was used.

Pellets were made from each of the four enamels and from compositions of the enamels containing 10 per cent of alumina. The enamel slips were dried and the dry enamels pressed into pellets with a 3/4-inch die. Three grams of enamel

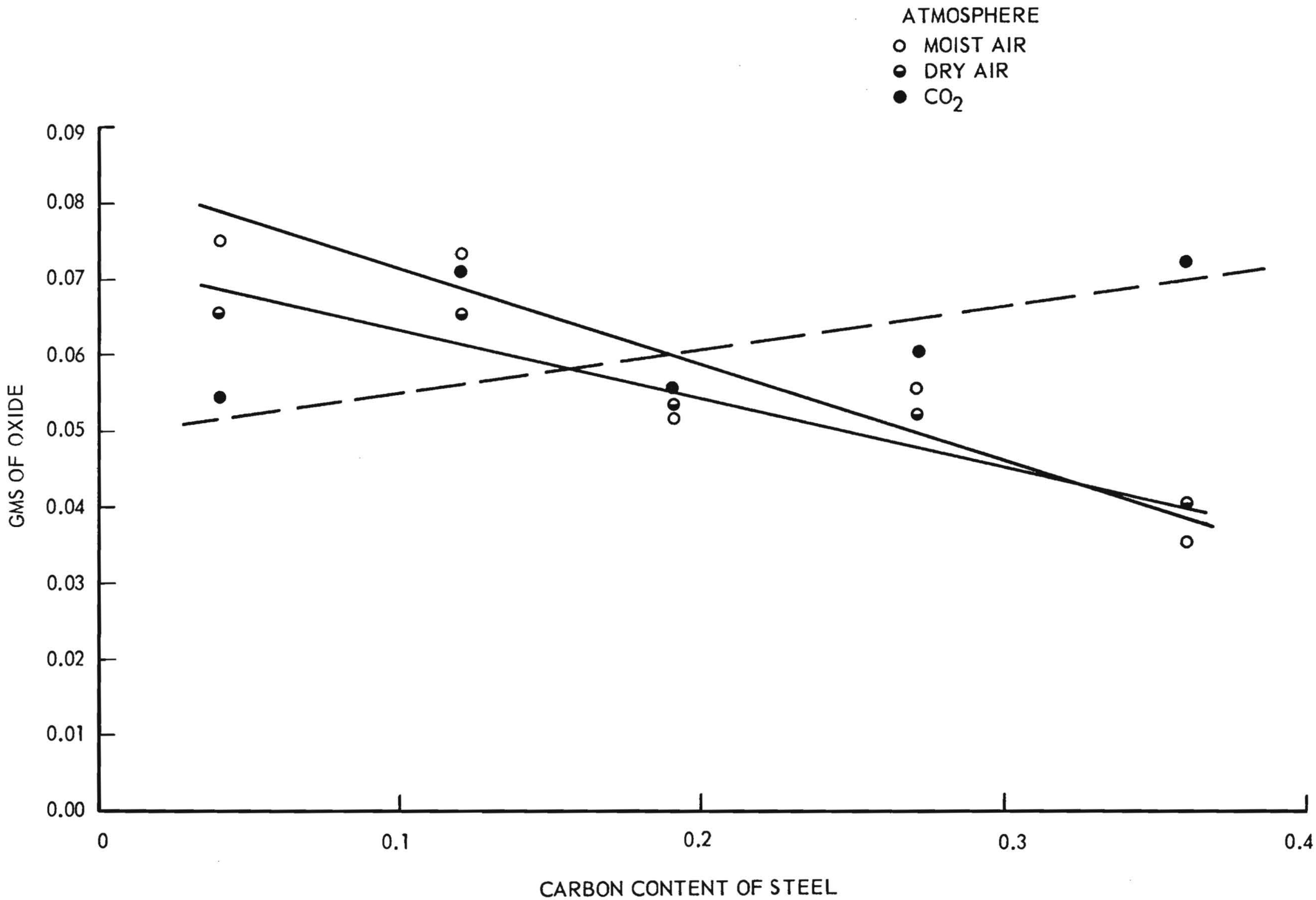

Figure 17. Oxidation Versus Carbon Content of Steel.

TABLE III

OXIDATION STUDIES ON STEELS
CONTAINING VARYING PERCENTAGES OF CARBON

Carbon Content	Air--Dry Atmosphere		Air--Wet Atmosphere		CO_2 Atmosphere	
	Wt of Steel	Wt of Oxide	Wt of Steel	Wt of Oxide	Wt of Steel	Wt of Oxide
(%)	(G)	(G)	(G)	(G)	(G)	(G)
0.04	102.0000	0.0615	103.0824	0.0803	104.1344	0.0457
0.04	104.0487	0.0703	101.3974	0.0701	103.5472	0.0539
0.12	92.4239	0.0594	91.6513	0.0710	88.8455	0.0714
0.12	95.0757	0.0714	90.3387	0.0768	92.2564	0.0709
0.19	97.1413	0.0534	96.8762	0.0458	100.9295	0.0619
0.19	98.4487	0.0539	98.3658	0.0579	101.1637	0.0494
0.27	95.1681	0.0521	95.4764	0.0576	101.2188	0.0598
0.27	93.5560	0.0422	95.4652	0.0547	93.8086	0.0612
0.36	98.9100	0.0390	99.1418	0.0306	92.2564	0.0825
0.36	98.9653	0.0422	101.0046	0.0408	101.2330	0.0626

and four drops of water were used to press each pellet at a pressure of 8000 psi. The pellets were placed on 2- by 2-inch sections of metal cut from steels with carbon contents ranging from 0.04 to 0.36 per cent. These steels had been previously sandblasted. Two samples of each steel were run with each enamel in both wet and dry atmospheres. The samples were fired in the same manner as in the oxidation tests. The spread of the pellet served as a measure of the wettability of the metal. The limits of reproducibility were greater than the spread of the enamel on various steels and the difference of spread in various enamels. For this reason no further time was devoted to this test.

G. Welding

1. Electrode Classification

In order to study possible defects in enamels on welds, it was first necessary to have these defects show up in welding studies. C1012 steel plates, 4- by 4- by 3/16-inch, were butt welded by the manual arc method utilizing an a-c arc welding generator to form a 4- by 8- by 3/16-inch sample. Previous coatings on T-joint specimens which were fabricated using AWS E 6016 Lo-Hydrogen electrodes had shown no defects in coatings on welds.

An attempt to produce fishscale was made by using a number of different welding electrodes of AWS classification. (See Table IV.) The AWS electrodes

TABLE IV

WELDING ELECTRODE INFORMATION

AWS Classification	Current	Position	Coating	Remarks
E6013	ac or dc Straight and reverse	All	High titania or potassium	
E6016	ac or dc Reverse	All	Lime or lime titania	Low Hydrogen
E6027	ac or dc Reverse	Horizontal and flat	Iron Powder	
E10013	ac or dc Straight	All	Mineral	This electrode is usually used with chrome molybdenum steels
E10016	ac or dc Reverse	All	Lime or lime titania	Low hydrogen

that caused fishscale were as follows: 6016, 10013, and 10016. The 10016 electrode caused the most fishscale directly on the weld. The 10013 class electrode gave fishscale on each edge of the weld. With this electrode the enamel came off the weld at the edge of the 1012 steel, leaving clean metal. Two plates were welded with electrodes of AWS 10013 classification. One plate was enameled with an enamel very susceptible to fishscale; the second plate was enameled with an enamel that does not ordinarily fishscale. The first plate fishscaled severely along the edge of the weld. The second plate had no fishscale whatsoever. The same procedure was used with the other electrodes that had shown tendencies to fishscale. With every electrode, enamels could be applied that would not fishscale (Table V).

Welding electrodes from various manufacturers were evaluated. All electrodes of the same AWS class acted in the same manner when enameled, regardless of manufacturer.

2. Welding Techniques

The effect of a poor weld on the coating properties of an enamel was tested.

Unsound or cold welds were made by depositing a bead of weld metal down the center of a 4- by 4-inch plate of C1012 hot-rolled steel. The back side of the plate was cooled during welding by a spray of water. The first plate was welded using a very low current which caused the arc to sputter and to go out several times in progressing across the plate. Two plates were welded at this current and at increasing currents until the recommended operating current for AWS 6013 electrodes was reached. One set of welded plates was cut into two 1-1/2- by 2-inch plates so that the weld metal formed the short axis of the sample.

TABLE V

TENDENCY TO FISHSCALE VERSUS WELDING ELECTRODE AND ENAMEL USED

Enamel	Mill Addition (Alumina)	6016	10013	10016
-D-		Yes	No	No
-D-	10% Calcined	No	No	No
-D-	20% Calcined	No	No	No
-D-	10% Fused	No		No
-D-	20% Fused	No	Yes	Yes
--A-		No	Yes	No
-A-	10% Calcined	No	No	No
-A-	20% Calcined	No	No	No
-A-	10% Fused	No		No
-A-	20% Fused	No		No
-A-	30% Fused	No		No
-A-	40% Fused	No		Yes
-B-		Yes	Yes	No
-B-	10% Calcined	Yes		No
-B-	20% Calcined	No		No
-B-	10% Fused	Yes	No	No
-B-	20% Fused	No		No
-S-		Yes		Yes
-S-	10% Calcined	No		No
-S-	20% Calcined	No		No
-S-	10% Fused	No	Yes	Yes
-S-	20% Fused	No		No

Gas extraction tests were run on these samples. (Table VI). Gas extracted seemed to be a function of the weld technique. More gas was extracted from sound welds containing no cavities or nonmetallic inclusions (normal current) than from welds containing cavities and inclusions (low current).

TABLE VI

GAS EXTRACTED VERSUS SOUNDNESS OF WELD

Welding Current	Fishscale on weld	Gas Extracted (Ml)
Low	None	0.37
Medium	None	0.60
Normal	None	1.55

The second set of plates was coated with an enamel susceptible to fishscale. These plates were set aside to observe for fishscaling.

The next attempt to form welds that would produce defects in enamels was to place materials in the weld that would form nonmetallic inclusions. The materials were placed between two plates of C1012 steel and AWS 6013 electrode used to butt weld the plates. Figure 18 is a micrograph of a weld area showing nonmetallic inclusions. No fishscale appeared on the enamel over this weld.

Since these experiments showed that welds containing cavities were receptive to porcelain enamel, attempts were made to alleviate the gas pressure by drilling holes in the weld. Holes 1/16 inch in diameter were drilled in welds 3/4 inch apart. Two plates were coated with each enamel, one plate with holes and one without. The holes did not seem to make any difference.

H. Gas Extraction Studies

Additional units of the gas extraction apparatus developed under Contract NObs 66521 were fabricated. Project Report No. 1 under the present contract

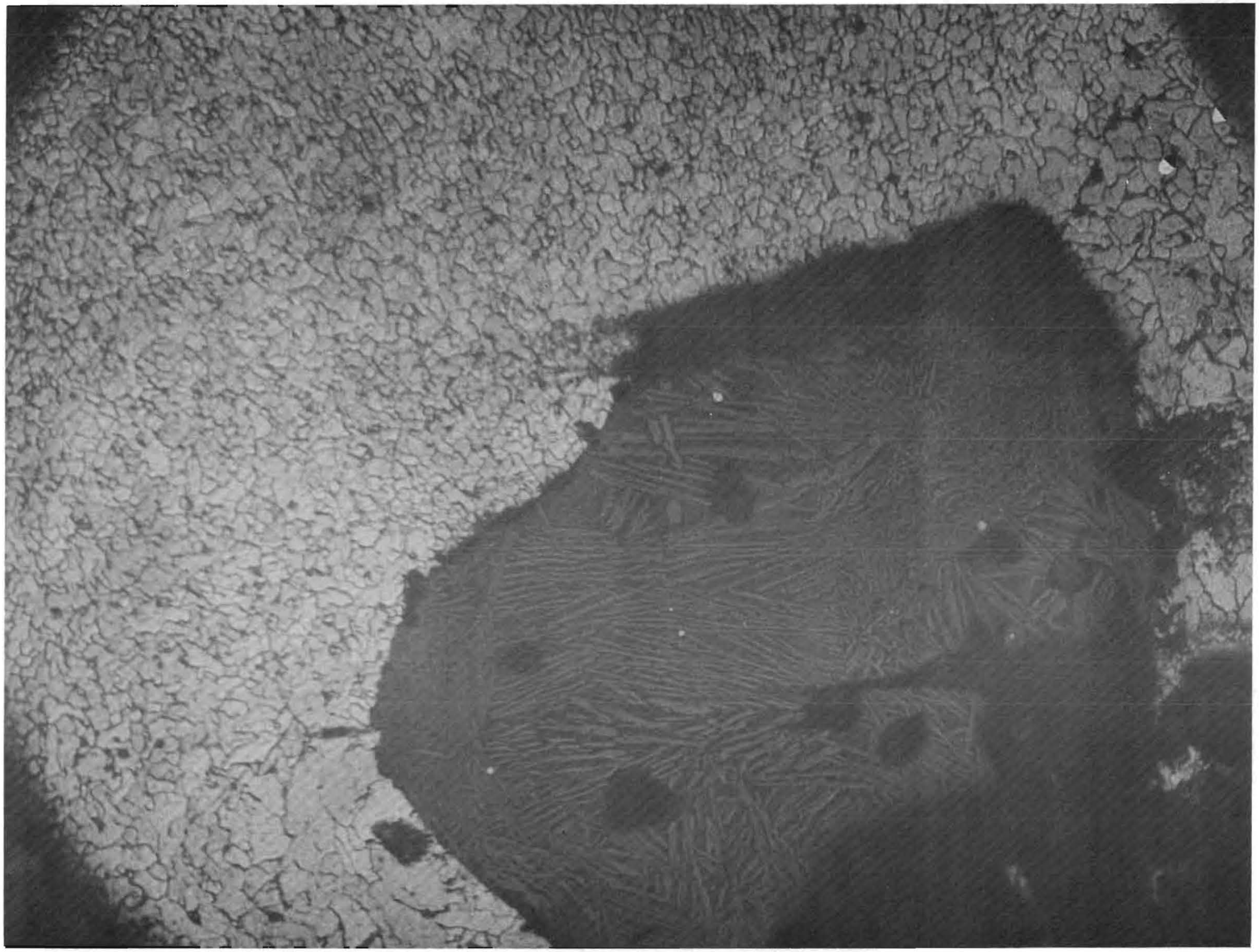

Figure 18. Micrograph of Weld Showing a Nonmetallic Inclusion. (223X).

was written describing the construction of this apparatus and its operation and is included as an appendix to this report.

Several possible variables were investigated before starting initial extraction operations on steels of carbon contents ranging from 0.04 to 0.36 per cent.

In an effort to obtain a quenching medium which would not react when steel was plunged into it at 1400° F, carbon tetrachloride was selected. Two samples of C1012 steel cut from the same stock were fired in an atmosphere of dry air for 22 minutes at 1400° F. One sample was quenched in carbon tetrachloride and the second sample was allowed to cool slowly in air. The sample quenched in carbon tetrachloride gave 0.41 ml of gas and the air cooled sample gave only 0.05 ml of gas. It is felt that the cooling action of the carbon tetrachloride was too slow to completely entrap all the hydrogen, yet the sample gave a much larger volume of gas than the other samples being quenched in water at this time. Therefore, it was felt that reactions were taking place which were forming gases other than hydrogen and these gases were being removed and collected in the extraction testing. Since quenching is used to entrap the hydrogen by rapidly cooling the enameled specimen while the coating remains essentially intact, it was decided that water would continue to be used as the quenching medium.

To determine if rusting on drying is a factor in gas extraction, two samples were enameled with the same enamel. One sample was allowed to dry in the open. The second sample was immediately put in the dryer after spraying and dried at 110° C. Both the samples gave 0.50 ml of gas, indicating that slow drying time causing the metal to rust was not a factor in gas extraction.

Two series of gas extraction tests were run. The initial or exploratory series of tests was run on five grades of 3/16-inch steel plate varying in carbon content from 0.04 to 0.36 per cent. The heat histories of these steels are found in Table VII. These tests were run with four ground coat enamels as obtained from four manufacturers and with these same four enamels containing 10- and 20-per-cent additions of fused alumina and 10- and 20-per-cent additions of calcined alumina. Due to the large number of tests, only two samples were run with each enamel.

TABLE VII

HEAT HISTORIES OF STEELS USED IN INITIAL FISHSCALING AND GAS EXTRACTION STUDIES

Carbon Content (%)	Mn (%)	P (%)	S (%)	Si (%)	Cu (%)	Al (%)	Source and Type
.05	.30	.015	.034	.015	.06	.039	-W-, Aluminum-killed
.07	.35	.009	.025	----	----	----	-W-, capped
.07	.25	.009	.026	----	----	----	-X-, hot-rolled, pickled and oiled
.16	.38	.012	.030	.06	.05	.009	-W-, silicon-semi-killed
.19	.47	.013	.028	----	----	----	-X-, hot-rolled
.24	.43	.012	.024	----	----	----	-X-, hot-rolled
.04	.37	.008	.030	.007	.10	.005	-W-, rimmed
.12	.40	.010	.031	----	----	----	-Y-, hot-rolled strip
.27	.47	.010	.029	.04	----	----	-X-, hot-rolled sheet
.44	.79	.026	.025	.23	----	----	-X-, hot-rolled sheet

From these preliminary extraction tests and the fishscale observations, it was concluded that a possible procedure for qualifying steel plate acceptably receptive to porcelain enamel coating could be established by the use of a "standard enamel" and by additions of fused alumina to this standard enamel.

In the preliminary testing it was noted that if a particular steel sample was coated with an enamel and a second sample of the same steel was coated with the same enamel containing a 10-per-cent addition of alumina, there was a difference in the amount of gas extracted. If the gas extracted from the steel was less when coated with the enamel containing the alumina addition than when coated with the pure enamel there would be fewer delayed fishscales on a sample of steel coated with the alumina-bearing enamel than on a sample coated with the same enamel without alumina. If coating a steel with the alumina-bearing enamel caused an increase in the amount of extractable gas, more fishscales occurred on the sample coated with the alumina-bearing enamel.

Only a few samples were run on each steel in the exploratory testing. In order to establish a better basis for qualifying steel, a large number of tests would have to be run.

For conclusive testing and establishment of a procedure for qualifying steel plate, a number of steels of 3/16- and 1/4-inch plate were obtained in sufficient quantity to insure a representative number of tests. (See Table VIII)

For more realistic testing, steels with unknown heat histories were obtained. Carbon content range and method of fabrication were the only data available on the steels.

TABLE VIII

STEELS OBTAINED FOR FINAL TESTING

Carbon Content Range (%)	Thickness (Inch)	Type	Source
0.1 - 0.2	3/16	Hot rolled plate	-Z-
0.1 - 0.2	1/4	Hot rolled plate	-Z-
0.15 - 0.2	3/16	Cold finished strip	-V-
0.3 - 0.4	3/16	Hot rolled plate	-Y-
0.3 - 0.4	1/4	Hot rolled plate	-Y-
0.4 - 0.5	3/16	Hot rolled plate	-Z-
0.4 - 0.5	1/4	Hot rolled plate	-Z-

One ground coat enamel† was selected for use as a "standard enamel," and is designated throughout this report as enamel "-S-". This ground coat enamel had the following composition.

Frit No.	Parts by Weight
S-1	65
S-2	15
S-3	20
	100

The mill addition was the same as that in Section B-1 of this chapter. Three other enamel compositions were made by adding 5, 10 and 15 per cent (by weight of the frit) of fused alumina to the standard mill addition.

Firing for all gas extractions was in the inconel chamber shown in Figure 1. The flexible stainless steel tube is attached to a 1/4-inch-diameter pipe

†Mill Batch Formulation on page 5.

which surrounds the inside perimeter of the bottom of the box. One-sixteenth-inch holes are drilled on one-inch centers in the side of the 1/4-inch-diameter pipe at an angle of 45° below horizontal and facing the center of the box. This allows any atmosphere desired to be supplied to the chamber.

Initial test samples were coated by spraying. It was necessary to support these samples by the edges during spraying, with the result that a very small bare spot was left on the metal.

The final group of samples was prepared by dipping into a slip with a specific gravity of 1.7. These samples were prepared by drilling a 1/16-inch hole in one corner and passing an inconel wire through the hole. The wire was used for support while dipping and firing a sample.

Initially, the gas extraction samples were placed on wire racks made from 4-mesh stainless steel screens. The fired samples, however, stuck to the wire racks, causing the enamel coating to break before quenching of the sample.

The wet atmosphere firings were provided by supplying air at a rate of 8 liters per minute through water at 25° C and then through the flexible stainless steel tube into the firing chamber.

The dry atmosphere firings were accomplished by passing air at a rate of 8 liters per minute through a calcium sulfate drying tube and then through sodium hydroxide flakes.

Extraction samples were placed in the chamber and the top of the chamber closed. The desired atmosphere was then pumped into the chamber for 10 minutes before placing the chamber in the furnace. Firing time for all tests was 22 minutes. Firing temperature for the initial series of tests was 1400° F. For the final series of tests, each set of samples was fired in a wet atmosphere and at the optimum maturing temperature of the enamel formulation used.

Figures 19 and 20 show the effects of atmosphere on gas extraction. The gas extraction procedure is the same as that described in Project Report No. 1, Contract NObs 72209. Table IX shows the results of the initial testing and Table X the results of the final testing using the "standard enamel."

I. Observation of Fishscale

In both the initial and final testing, two series of test plates 4- by 4- by 3/16-inch were coated and fired with each enamel coating used for gas extraction. One series of test plates was set aside at room temperature and observed periodically for fishscaling for a period of several weeks. The second series of test plates was placed in a dryer at 175° C for a period of 48 hours and then the temperature of the dryer raised in 50° increments each 48 hours until a temperature of 425° C was reached. Observations for fishscale were made after each 48-hour period. Tables XI and XII show the results of these tests.

Tables IX and XI cannot be easily compared to bear out the theory that if the addition of alumina to an enamel caused an increase in extractable gas content there is also an increase in fishscale and conversely if the addition of alumina causes a decrease in extractable gas there is also a decrease in fishscale because the only common steel in the two tables is the 0.19 per cent carbon.

Tables X and XII can be more easily compared because the same type steels were used in both tests. For easier comparison with Table X, a plus sign(+) has been added to Table XII if the addition of alumina to the standard enamel caused an increase in extractable gas and a minus sign(-) if the addition of alumina caused a decrease in extractable gas.

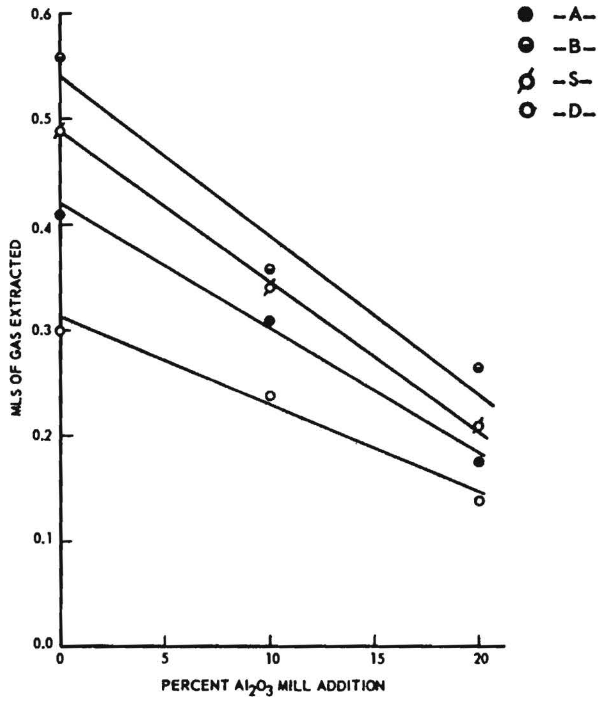

Figure 19. Gas Extracted for Wet Atmosphere Firings.

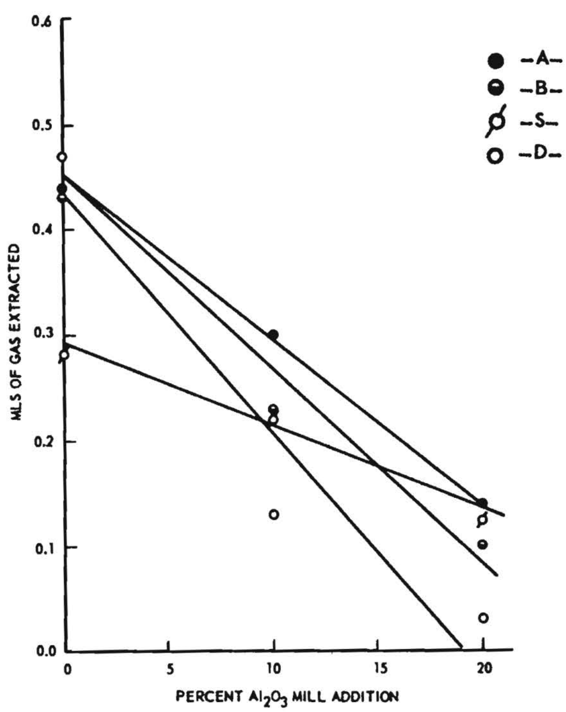

Figure 20. Gas Extracted for Dry Atmosphere Firings.

TABLE IX

GAS EXTRACTED FROM STEELS IN INITIAL TESTING
(3/16-INCH PLATE THICKNESS)

Carbon Content of Steel (%)	-D- (Ml)	-D- with 10% Alumina (Ml)	-A- (Ml)	-A- with 10% Alumina (Ml)	-B- (Ml)	-B- with 10% Alumina (Ml)	-S- (Ml)	-S- with 10% Alumina (Ml)
0.04	0.20	0.03	------	0.25† (.40 .10)	0.20	0.47††	0.27† (.10 .44)	0.06
0.12	0.46	0.13	0.39	0.30	0.42†	0.23	0.28	0.22
0.19	0.12	0.03	0.04	0.10	0.03	0.50† (.67 .35)	0.16	0.27
0.27	0.25††	0.22††	0.51††	0.07††	0.42††	0.05††	0.60††	0.10††
0.44	0.32	0.22† (.39 .05)	0.18† (.30 .06)	0.10	0.40	0.22† (.40 .05)	0.26	0.12

Note: Two samples were run for each enamel, except as indicated, with maximum variation between samples being 0.15.

†Variation greater than 0.15. Number in parenthesis shows variation.

††One sample only.

TABLE X

GAS EXTRACTIONS IN FINAL TESTING SHOWING THE EFFECT OF ALUMINA ADDITIONS TO THE STANDARD ENAMEL

Carbon Content of Steel	Source	Thickness	Alumina 0%	Alumina 5%	Alumina 10%	Alumina 15%
(%)		(Inch)	(Ml)	(Ml)	(Ml)	(Ml)
(0.1 - 0.2)	-Z-	3/16	.37	.28-	.14-	.19-
		1/4	.21	.34+	.28+	.26+
(0.15 - 0.2)	-V-	3/16	.35	.36	.47+	.46
(0.3 - 0.4)	-Y-	3/16	.55† (.38/.65)	.31	.35-	.44
		1/4	.20	.29+	.22+	.31† (.46/.75)
(0.4 - 0.5)	-Z-	3/16	.38	.29	.33-	.25
		1/4	.58	.42-	.35-	.29

†Variation greater than 0.15. Number in parenthesis shows variation.
Note: Enamel -S- was used as Standard Enamel.

TABLE XI

TENDENCY TO FISHSCALE VERSUS CARBON CONTENT
OF STEELS IN INITIAL TESTING

Carbon Content of Steel	Enamel -A-	Enamel A + 10 % Calcined Alumina	Enamel B + 10 % Fused Alumina	Enamel B + 20 % Fused Alumina	Enamel D + 10 % Fused Alumina	Enamel D + 20 % Fused Alumina	Enamel D + 20 % Calcined Alumina	Enamel -S-	Enamel S + 10 % Fused Alumina	Enamel S + 10 % Calcined Alumina	Enamel S + 20 % Calcined Alumina
0.05	F2	N	F1	N	F1	F1	F2	F1	N	F1	N
0.07†	F1	N	F1	N	F1	F1	F1	N	N	N	N
0.07††	F2	F2	F1	N	F1	F1	F2	F1	N	N	N
0.16	F2	F1	F1	F1	F1	F1	F2	F1	F1	F1	N
0.19	F2	F1	F1	F1	F1	F1	F2	F1	F1	F2	N
0.24	F2	F2	F1	F1	F1	F2	F2	F1	F1	F1	N

Note: These were the only enamels tested due to the short supply of steel. The B and D enamels were not included.

†Capped Steel.

††Hot rolled, pickled and oiled.

F1 = Slight Fishscale.

F2 = Severe Fishscale

N = No Fishscale

TABLE XII

TENDENCY TO FISHSCALE VERSUS CARBON CONTENT OF STEELS IN FINAL TESTING. ALL STEELS COATED WITH ENAMEL -S-

Carbon Content of Steel (%)	Source	Thickness (Inch)	Alumina 0%	5%	10%	15%
(0.1 - 0.2)	-Z-	3/16	F2	F1-	F1-	N-
		1/4	F1	F2+	F2+	N+
(0.15 - 0.2)	-V- Cold Finished	3/16	F1	N	N+	N+
(0.3 - 0.4)	-Y-	3/16	F1	F2-	F2-	N-
		1/4	N	N+	N+	N+
(0.4 - 0.5)	-Z-	3/16	F2	F1-	N-	N-
		1/4	F1	F2-	F1-	N-

N = No Fishscaling.
F1 = Slight Fishscaling.
F2 = Severe Fishscaling.
\+ = Indicates an increase in extractable gas with addition of alumina (Table IX)
\- = Indicates a decrease in extractable gas with addition of alumina (Table IX)

IV. DISCUSSION

A. Enamel Variables

1. Bubble Structure

Many factors, such as firing temperature, firing time, grinding fineness and thickness of coating, enter into the formation of bubble structure; each of these factors was investigated for each enamel and the relative weight of each factor established. None of the above factors, however, influenced the formation of bubble structure as much as the type of clay used.

It is generally accepted that bubble structure is an important factor in determining whether an enamel will fishscale when applied to a metal. Figures 2, 3, 4, 5, 6, 7, 8 and 9 show that tendency to fishscale and bubble structure cannot be determined from batch to batch of enamels even when raw materials are provided by the same manufacturer. Figures 8 and 9 show the bubble structure of Clay No. 1-a and 1-b. In Figure 8 it can be seen that the bubbles are uniform and close together and the enamel is transparent. In Figure 9 the bubbles are about the same size, but are not as close together; also "muddy areas" can be seen between the bubbles and adjacent to the steel. These "muddy areas" are similar to those shown in Figures 14 to 23 of Annual Report No. 1, Contract NObs 66521. The cause of these "muddy areas" is not completely understood but they must contribute in some way to fishscaling since almost all enamels that show these "muddy areas" tend to fishscale. Moore[†] found that vacuum melted enamels did not show these "muddy areas" and concluded that they are caused by a reaction between the dissolved water in the coating and the steel base. Since

[†] D. G. Moore and M. A. Mason, "Investigation of Gases Evolved During Firing of Porcelain Enamels," J. Amer. Cer. Soc., 36, 241-249 (1953).

the same frits were used with two different clays, it is felt that water in the clay may have had some effect in causing these "muddy areas." Also, frit numbers and compositions are subject to change as is evidenced by Manufacturer -A's- change of frit numbers.

2. Alumina Mill Additions

It has been previously shown that bubble structure is largely dependent on firing time and temperature. These variables must be very closely controlled if the proper bubble structure is to be obtained. Figures 7 and 9 show bubble structures of the same enamel from two different mills using the same ingredients. These samples were fired for the same length of time but in different furnaces. The difference in development of bubble structure can be readily seen. A more reliable method of controlling enamel defects is needed. A better method of controlling enamel defects would not depend on bubble structure. Small additions of alumina have shown a tendency to reduce fishscale and larger additions have almost completely eliminated it. At the same time adherence and thermal shock resistance have been greatly improved. Figure 21 is a micrograph of an enamel containing a 20-per-cent addition of calcined alumina. It can be seen that the alumina particles have almost completely replaced the bubbles. It is believed that these alumina particles function as bubbles(act as a void) in contributing to thermal shock resistance and at the same time reducing fishscaling.

Of all the mill additions tested, alumina consistently gave the best results. Fused alumina is preferred over calcined alumina because the fused alumina acts in a similar way to the calcined alumina, yet does not require as high a firing temperature, gives much smoother enamel surfaces and has been found to be less conducive to tearing.

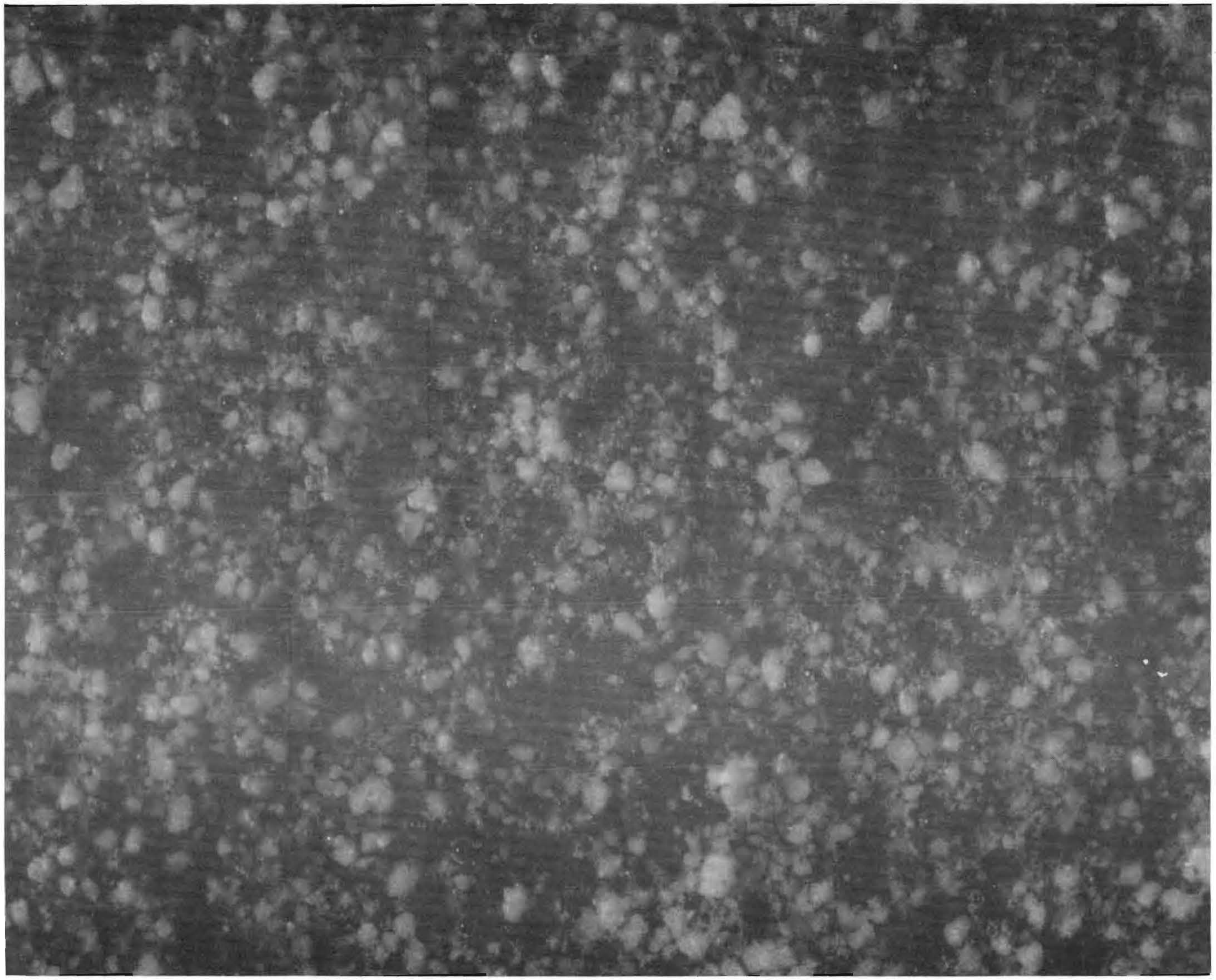

Figure 21. Bubble Structure of Enamel Containing 20 Per Cent Calcined Alumina. (60X).

B. Tearing

The use of alumina as a mill addition is limited in that other problems are introduced by its use. Dipping of T-sections into enamels containing large percentages of alumina (20 per cent) introduced a draining problem. Firing of these T-sections caused a tearing problem where thick sections joined thin sections. The tearing test described under Part D of the experimental procedure was not intended to replace the T-joint test but was used to supplement it and conserve metal and time in that test samples could be prepared and fired in a much shorter period of time than in the T-joint test.

Additions of calcined alumina greater than 10 per cent gave tearing with most enamels tested; however, additions of fused alumina up to 40 per cent were made with one enamel with only slight tearing. Although the reasons for fused alumina being less conducive to tearing than the calcined alumina are not completely understood, it could possibly be due to the green strength of the enamel. Calcined alumina has a tendency to pick up moisture and the loss of this moisture upon the quick heating of the enameled specimens could very easily disrupt the structure of the coating, which would not be fluid enough to heal over on the slower heating thick sections.

C. Adherence and Thermal Shock

As mentioned previously, the additions of alumina up to 10 per cent greatly improve adherence and consequently thermal shock resistance. Tests run with calcined alumina showed an increase in adherence up to 10-per-cent additions with three enamels and up to 20-per-cent additions with one enamel. The difficulties with tearing tests with the larger additions of alumina may in some way be related to the adherence difficulties experienced with the addition of alumina greater than 10 per cent.

Although a definite relationship between carbon content of steel and oxidation rate was established, the variables in the adherence tests were too large to establish a definite relationship between adherence and carbon content of steel.

Other factors may enter into adherence and thermal shock resistance. A difference in cooling rate in air of two unlike steels of the same thickness was noted. Two 4- by 4- by 3/16-inch sections, one C1012 and the other C1044 were welded together to form a 4- by 8-inch section. This section was heated to 1400° F. Upon removal from the furnace the high carbon end cooled at a faster rate and had lost all radiant heat while the low carbon end was still glowing red. Conditions might be encountered in service which would cause only one side of an enameled section to be cooled at once.

To avoid the "steam" effect and to cool only one side of a sample the spray test described in the procedure was devised in an effort to impose more severe conditions on the test samples. The test samples shocked in this manner became "sandy" much quicker than those immersed in water. However, all enamels tested passed the thermal quench test with the proper mill addition of alumina.

D. Welding

The welding study revealed that with proper selection of welding electrode and normal care in welding technique, a weld can be enameled successfully if the adjoining metal can be coated successfully. The study revealed that welds containing cavities and nonmetallic inclusions were more receptive to enamels than sound welds. This was probably due to the fact that occlusions in the welds form reservoirs and alleviate the gas pressure.

E. Gas Extraction

It is thought that the majority of enamel defects are caused by entrapped gases in metals. These gases are charged into the metals during fabrication and during enameling. The gas extraction apparatus was developed to measure these gases and possibly relate the volume extracted with enamel defects.

For each enamel and steel composition tested, a like 4- by 4-inch sample was coated and fired under the same conditions and set aside for observation of fishscale.

Figures 17 and 18 show the effects of wet and dry atmospheres on a C1012 steel with various enamels. In all cases, there was decrease in gas extracted as the alumina content was increased. Observation of fishscale showed a decrease in each case. The -S- enamel was selected as a "standard" enamel for comparison of fishscale observation and gas extraction measurements. The preliminary tests with the -S- enamel showed that the addition of alumina caused an increase in the amount of gas extracted with some steels (Table IX) while others reacted in the opposite way. This set up the basis for a possible test for qualifying steels.

If the additions of alumina caused an increase in the amount of gas extracted, there was a corresponding increase in fishscaling. If the addition of alumina caused a decrease in extractable gas, fishscaling also decreased. If the column headed 10% alumina in Table XII is compared with the same column in Table X, it can be seen that except for the cold-rolled steel and the -Y- steel that the above hypothesis is true. In the case of the -Y- steel experimental error in gas extraction with the standard enamel was so great that these results can be disregarded. It is also understood that cold-rolled steel is practically never specified for shipboard use.

Five-per-cent addition of alumina decreased fishscaling little or not at all. This absence of effect on fishscaling could result from the lack of enough particles of alumina to act as bubbles in the structure of the enamel.

V. CONCLUSIONS

Based on the work under this contract and Contract NObs 66521, it is felt that steel plate and weldments can only be qualified by the use of a "standard enamel." This standard enamel would have to be controlled by having a large quantity of frit on hand at a Naval Laboratory or readily available from the Bureau of Standards. Past experience has shown that commercial frits cannot be used because of the policy of changing frit numbers. Also the unwillingness of frit manufacturers to release smelt batch compositions to the Government because of proprietary interests would make close control of variables impossible.

The clay used as a mill addition in the enamel would also have to be controlled very carefully. Experience under this contract has shown that clays obtained by the same brand and number are not consistent in their bubble-forming characteristics and therefore change the tendency of an enamel to fishscale. Tests with three different clays from one manufacturer have shown that the formation of bubble structure plays a large part in the tendency of an enamel to fishscale. The lack of formation of a proper bubble structure to resist fishscaling can be somewhat overcome by alumina additions to the mill batch. It is believed that the alumina particles act in a manner similar to the bubbles in the bubble stratum in that they form voids in the enamel.

For purposes of this investigation, accelerated fishscaling was satisfactorily accomplished by holding coated test panels at 175° C for 24 hours.

It is believed that to a significant degree, the factors attributable to the steel plate enamel system responsible for defective coated parts intended to conform to specification Mil P-16961-B have been assessed, the principal factor being extractable gas.

A. Gas Extraction

Results of this investigation indicate the possibility that the gas extraction test is valid as a criterion for qualifying steel whereby if more than a maximum allowable amount of gas was extracted the plate would be likely to fishscale and, conversely, if less than a maximum amount of gas was extracted the plate would not be likely to fishscale. Results to date are inconclusive.

The following hypothesis was studied through preliminary tests: if the addition of alumina to a standard enamel caused a decrease in extractable gas, there would be a corresponding decrease in fishscaling and, conversely, if the addition of alumina caused an increase in extractable gas there would also be an increase in fishscaling. The majority of steels tested acted in the expected manner except for cold finished steel. In one instance tests with a hot rolled steel did not act in the expected manner. The range of gas extraction values for this steel was very large and the assignable cause for this variation was not determined. It is felt that this variation was possibly due to the steel, but since only a limited number of tests were run there is a possibility that the variation could be due to the gas extraction technique.

B. Thermal Shock

The T-joint thermal shock test as outlined in Mil P-16961-B is more than adequate; however, a more severe test was provided by spray cooling on one side of an enameled section only. The continual spray of cold water eliminated the "envelope" of steam which is formed around a section of metal which is immersed completely in water and therefore the sample was cooled much faster. Samples subjected to the spray tests failed quicker than metal sections completely immersed in water. Additions of alumina up to 20 per cent improved thermal shock resistance. The four enamels as received passed the thermal shock test on C1012 steel as outlined in Mil P-16961-B, but after shocking, the coatings were sandy to the touch and had a frosty appearance. The four enamels did not pass thermal shock tests on C1044 steel. The best thermal shock resistant coatings obtained were those containing from 7-1/2 to 10 per cent of alumina. The percentage of failure by thermal shock of enamels over welds was very small; in most cases the coating over the welds remained in better condition than the coating on the adjoining steel.

C. Tearing and Hairlining

Increasing the amounts of alumina in the mill addition while increasing adherence also caused a greater incidence of tearing defects. Additions of fused alumina proved less conducive to tearing than calcined alumina and at the same time were just as effective in increasing thermal shock resistance.

The supplemental test devised to bring out these defects did not prove to be of any advantage over the T-joint test other than that the samples could be fired quicker and were less bulky to handle.

D. Adherence

The adherence test as described in this report gave no definite relationship between the carbon content of steel and the enamel applied to it but showed that increasing the alumina content of an enamel resulted in improved adherence.

E. Oxidation of Steel

Studies indicated that there was a definite relationship between carbon content of steel and oxidation rate but experimental error gave too wide a range to establish a definite relationship between carbon content and adherence.

F. Wettability of Steel

The wettability study as carried out proved to be of no significant value.

G. Welding

Welds made by normal welding techniques were enameled successfully with any enamel that could be successfully applied to the adjoining metal.

Respectfully submitted:

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VI. APPENDIX

Reproduction of
PROJECT REPORT NO. 1
PROJECT NO. A-308

(As revised to meet
Government Specifications)

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

PROJECT REPORT NO. 1

PROJECT NO. A-308

GAS EXTRACTION APPARATUS

CONSTRUCTION AND OPERATION

By

J. D. Walton

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CONTRACT NO. NObs 72209
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DEPARTMENT OF THE NAVY

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

DECEMBER, 1956

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This report contains 16 pages.

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LIST OF FIGURES

I. CONSTRUCTION OF APPARATUS

The apparatus shown in Figure 1 is that used for extracting gas from steel, and consists of three basic components: gas burette, extraction chamber and base plate.

A. Construction of Gas Burette

The gas burette was made from two commercially available parts (Figure 2). The basic burette was obtained from Vendor -G- and is graduated in 0.05 ml divisions from 0-4 ml, in 0.2 ml from 4-15 ml and in 1.0 ml from 15-30 ml. The base of this burette is furnished with a small glass tube which was removed for our use and a 14/35 standard tapered female joint[†] was welded in its place.

B. Construction of Extraction Chamber

In Figure 3 the glass components of the upper portion of the extraction chamber are shown. The upper portion of the extraction chamber is composed of two items, a 6-inch length of 1-inch diameter Pyrex "Double-Tough" pipe and a 14/35 standard tapered male joint (-K- No. 6540). The 6 inch length of pipe was divided into two 3-inch lengths, each with one flared end. The unflared end was flame worked until it was reduced to the diameter of the straight end of the standard tapered male joint. This joint was then welded to the previously described 3-inch section of pipe, forming a section with a standard tapered 14/35 male joint on one end and a flared end of a standard 1-inch Pyrex pipe on the other. The lower portion of the chamber is composed of a Pyrex "Double-Tough" 2- by 1-inch pipe reducer[††] (Figure 4).

[†] -H-, No. J1906 (-K- No. 6540).

[††] -K-

All of the components necessary to assemble the extraction chamber are shown in Figure 4. The flanges used to join the two glass components are standard flanges with molded inserts used to join sections of 1-inch diameter Pyrex "Double-Tough" pipe. The gasket between the pipe sections is a Teflon type-T gasket, also a stock item for 1-inch diameter pipe.

C. Construction of Base Plate

The base plate to which the extraction chamber was sealed is shown in Figure 5. Figure 6 shows the blueprint for constructing the base plate. The plate was constructed from one piece of 4- by 4-1/4-inch stainless steel plate. Three holes were drilled, forming an equilateral triangle with sides of 3-3/8 inches, measuring from the center of each hole. The center of the index hole was located midway along one side of the plate 5/16 inch from the edge. The other two holes were located the same distance from the edge of their respective sides. These holes were tapped to receive 1/4-inch- 20 x 1-1/2-inch threaded studs. Three of these studs were screwed into the base plate flush with the back of the plate and silver-soldered in this position.

Into these holes stainless steel rods the same size as the holes were inserted flush with the bottom of the base plate and extending up through the top of the plate 1-1/4 inches. These stainless steel rods were silver-soldered to the bottom of the base plate.

On a chord drawn through any point 1/4 inch from the center of the circle described by the studs, and drawn perpendicular to a line connecting that point and the center of the circle, two 1/8-inch diameter holes were drilled, each 5/8 inch from the perpendicular. On the opposite side of the center from the chord, a 1/16-inch diameter hole was drilled 1/4 inch from the center.

The extraction chamber was secured to the base plate by means of a flange and molded insert designed for fastening 2-inch diameter Pyrex pipe sections. In this instance, the studs in the base plate extended through the flange, and 1/4-inch nuts were used to tighten the chamber against the plate. A Teflon type-T gasket available for 2-inch diameter Pyrex pipe was used to effect a seal between the extraction chamber and base plate.

D. Assembly of Three Main Components

Figure 7 shows the complete assembly of the apparatus.

II. ACCESSORY EQUIPMENT

Figure 8 shows the accessory equipment used in filling the apparatus. The 250-ml Erlenmeyer flask (-K- No. 5000) was used to hold the mercury for each extraction setup when the apparatus was not in use. The small long-stem funnel (-K- No. 6160) was used to fill the extraction setup with mercury and the 250-ml separatory funnel (-K- No. 6400) was used to separate the mercury from the butylphthalate after an extraction was made. The large short-stem funnel was used to filter the butylphthalate after each run to be sure that it remained clean.

TABLE I

REQUIRED MATERIAL

Quantity	Description	Vendor
1	Gas burette, No. J1906 graduated in 0.05 ml divisions from 0-4 ml, in 0.2 ml from 4-15 ml, and in 1.0 ml from 15-30 ml	-G-
1	Ground glass joints. Standard taper Pyrex glass No. 15821 (-K- No. 6540)	-H-
1	3-foot length Polyethylene tubing, 1/4-inch inside diameter, 1/16-inch wall thickness	-H-
1	250-ml Erlenmeyer flask Pyrex glass with 24/40 standard taper joint and stopper No. 13686 (-K- No. 5000)	-H-
1	250-ml pear-shaped separatory funnel Pyrex glass. Standard taper stopper No. 16, stopcocks No. 2. No. 14376 (-K- No. 6400)	-H-
1	Funnel, long stem exact 60° Pyrex glass 65-mm diameter, 150-mm stem length. No. 14171 (-K- No. 6160)	-H-
1	Funnel, short stem 125-mm diameter, 125-mm stem length No. 14146	-H-
6 feet	Extra heavy wall, rubber tubing, 1/4-inch inside diameter, 3/16-inch wall thickness No. 23496	-H-
1	Leveling bulb, Kimbel "K" brand 250 ml with vertical side tube connected at top and bottom	-J-
1	Pyrex "Double-Tough" pipe reducer, 2-inch x 6-inch length Pyrex "Double-Tough" pipe, 1-inch diameter	-K-
2	Molded inserts for 1-inch pipe	-K-
1	Molded insert for 2-inch pipe	-K-
2	Standard flanges for 1-inch pipe	-K-
1	Standard flanges for 2-inch pipe	-K-
1	Teflon type-T gasket for 1-inch pipe	-K-

(Continued)

TABLE I (Concluded)

Quantity	Description	Vendor
1	Teflon type-T gasket for 2-inch pipe	-K-
3	5/16-inch, 18- x 1-1/2-inch bolts	-K-
3	5/16-inch, 18-nuts	-K-
1	4 x 4 x 1/4-inch stainless steel plate	
3	1/4-inch-20 x 1-1/2-inch stainless steel studs	
3	1/4-inch-20 stainless steel nuts for studs	
1	450-watt, 115-volt hot plate, No. 61725	-E-
1	Vacuum Pump	-F-

III. OPERATION

A. Uncoated Metal

If the metal to be studied is uncoated, no pretreatment of the specimen is required unless heavy scale is to be removed. This may be done by light sandblasting--only enough blasting to remove lightly adhering scale.

A 2- x 1-1/2-inch specimen is used in this apparatus. The specimen is placed on the base plate, with one side against the 1/16-inch rod, and the other side against the two 1/8-inch rods. The 2-inch dimension of the specimen is perpendicular to the base plate.

The Teflon gasket is then placed on the bottom of the extraction chamber and the chamber is placed over the specimen and secured in this position by means of the 1/4-inch-20 nuts. The seal should be sufficient at this point to keep the mercury from leaking when put into the extraction chamber.

Mercury is poured into the extraction chamber until the level of the mercury reaches the necked-down portion of the 2- x 1-inch Pyrex pipe reducer.

One end of the 6-foot length of heavy wall rubber tubing is then slipped over the 14/35 standard taper joint on the top of the extraction chamber. The other end of this tubing is connected to a vacuum pump. A vacuum of 3 mm of mercury is applied to the system to remove all entrapped gases. The 1/4-inch-20 nuts are tightened sufficiently to reduce leakage to no more than one bubble every 5-10 seconds. The vacuum is then removed and the remainder of the chamber filled with butylphthalate.

The gas burette is placed on the extraction chamber and approximately 150 ml of butylphthalate is poured into the leveling bulb with the height of the bulb kept below the top of the extraction chamber.

With the stopcock on the top of the gas burette open, the leveling bulb is raised until the level of the butylphthalate reaches the top of the glass tube within the lower portion of the gas burette. This level is increased until the butylphthalate runs down the tube and fills the volume between the top of the extraction chamber and the lower portion of the gas burette. If the butylphthalate level were raised before the volume were filled, it would bridge over the top of the small tube, trapping air in this space. Once this volume is filled, the leveling bulb is raised until the entire gas burette is filled and butylthalate rises into the neck above the stopcock. The stopcock is then closed. The leveling bulb is then hung in a convenient location and the apparatus is placed on a hot plate.

The hot plate is adjusted to provide a constant mercury temperature of 175° C. Heating is continued until all gases have been expelled from the metal. No gases are assumed to remain when no bubbles are seen over a period of 30 minutes.

When recording the volume of gas liberated, it is advisable to tilt the apparatus carefully, first to one side and then to the other, to insure the liberation of any bubbles which might be trapped under the metal or between the metal and the walls of the extraction chamber.

After the extraction operation has been completed, the apparatus is allowed to cool. The leveling bulb is lowered to a position below the extraction chamber, and the stopcock on the gas burette is opened. All the butylphthalate is thus drained from the gas burette and the burette is removed.

The liquid contents of the extraction chamber are poured into a separatory funnel and the apparatus is dismantled. The mercury is drained from the separatory funnel into a glass stoppered Erlenmeyer flask. The butylphthalate is then drained through a funnel and filtered into another flask for storage.

B. Coated Metal

When a ceramic-coated metal is to be studied with respect to the hydrogen injected into it through the enameling operation, the following procedure is followed:

The metal is prepared for coating by sandblasting. The coating is applied by spraying or dipping and fired under the specified conditions. When the specimen is removed from the furnace it is immediately plunged into ice water. As soon as the specimen is cool it is again sandblasted to remove all traces of coating and is immediately set up in the extraction apparatus as previously described.

Respectfully submitted:

J. D. Walton
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

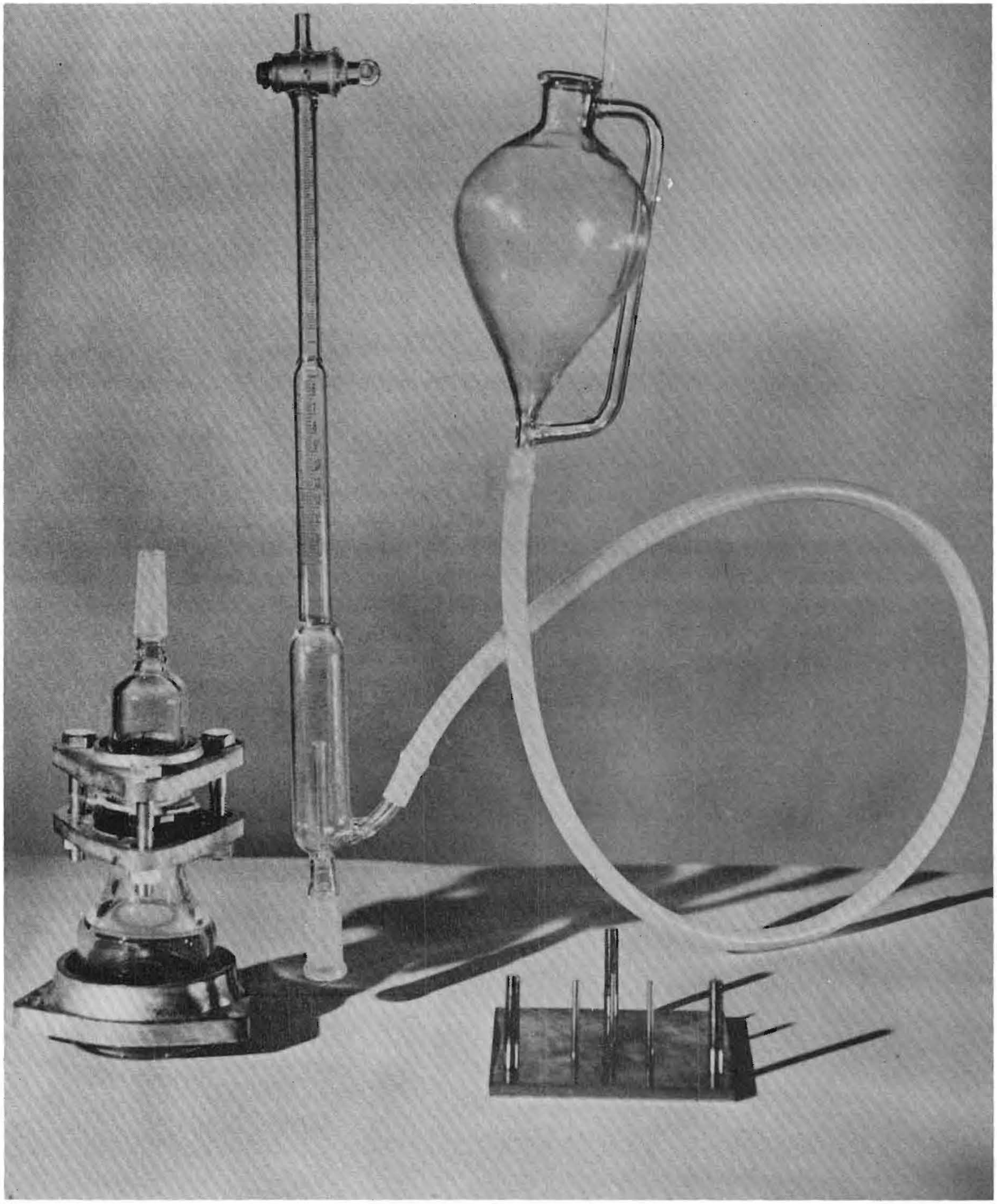

Figure 1. Basic Components of Extraction Apparatus.

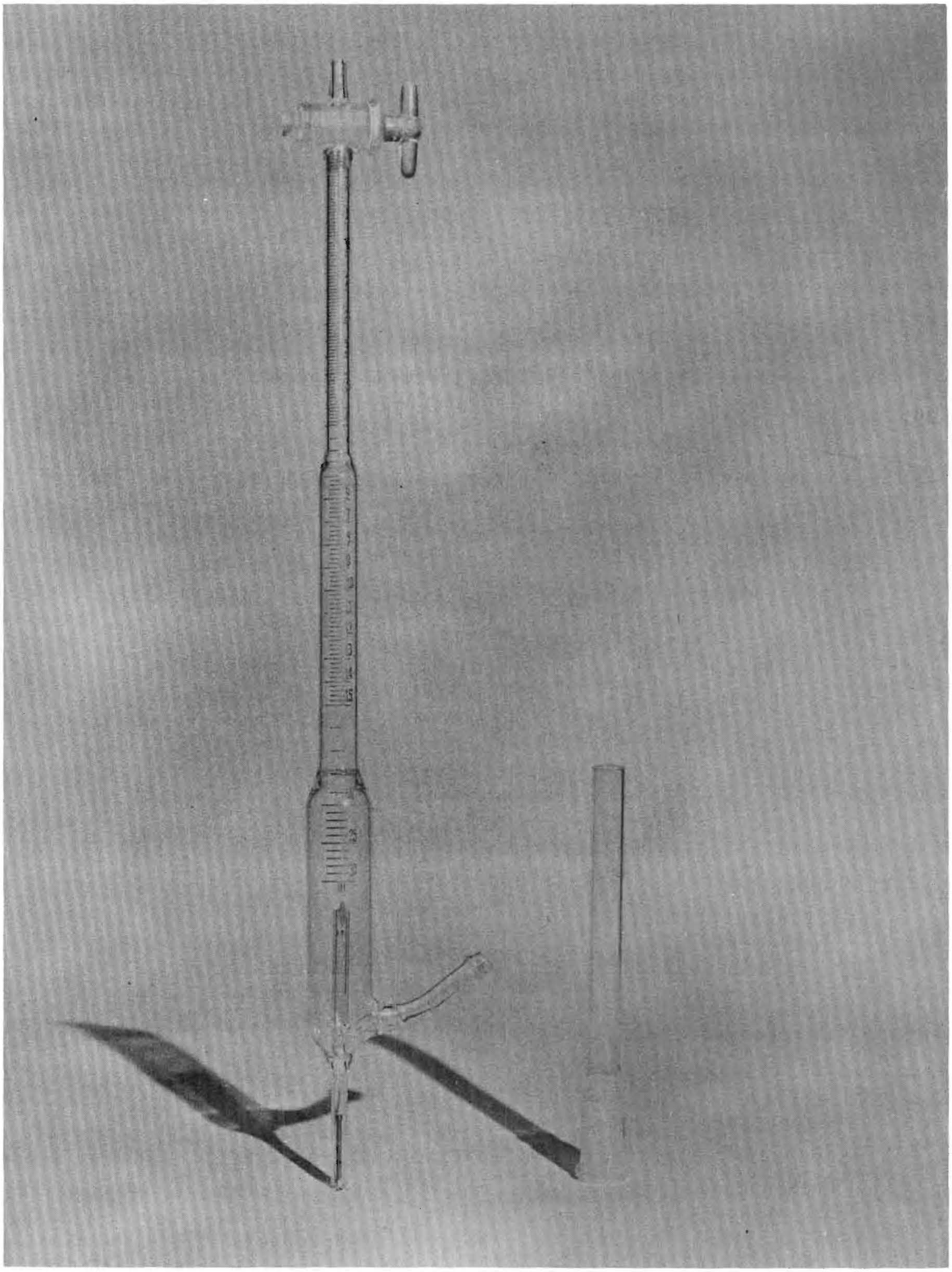

Figure 2. Basic Components for Construction of Gas Burette.

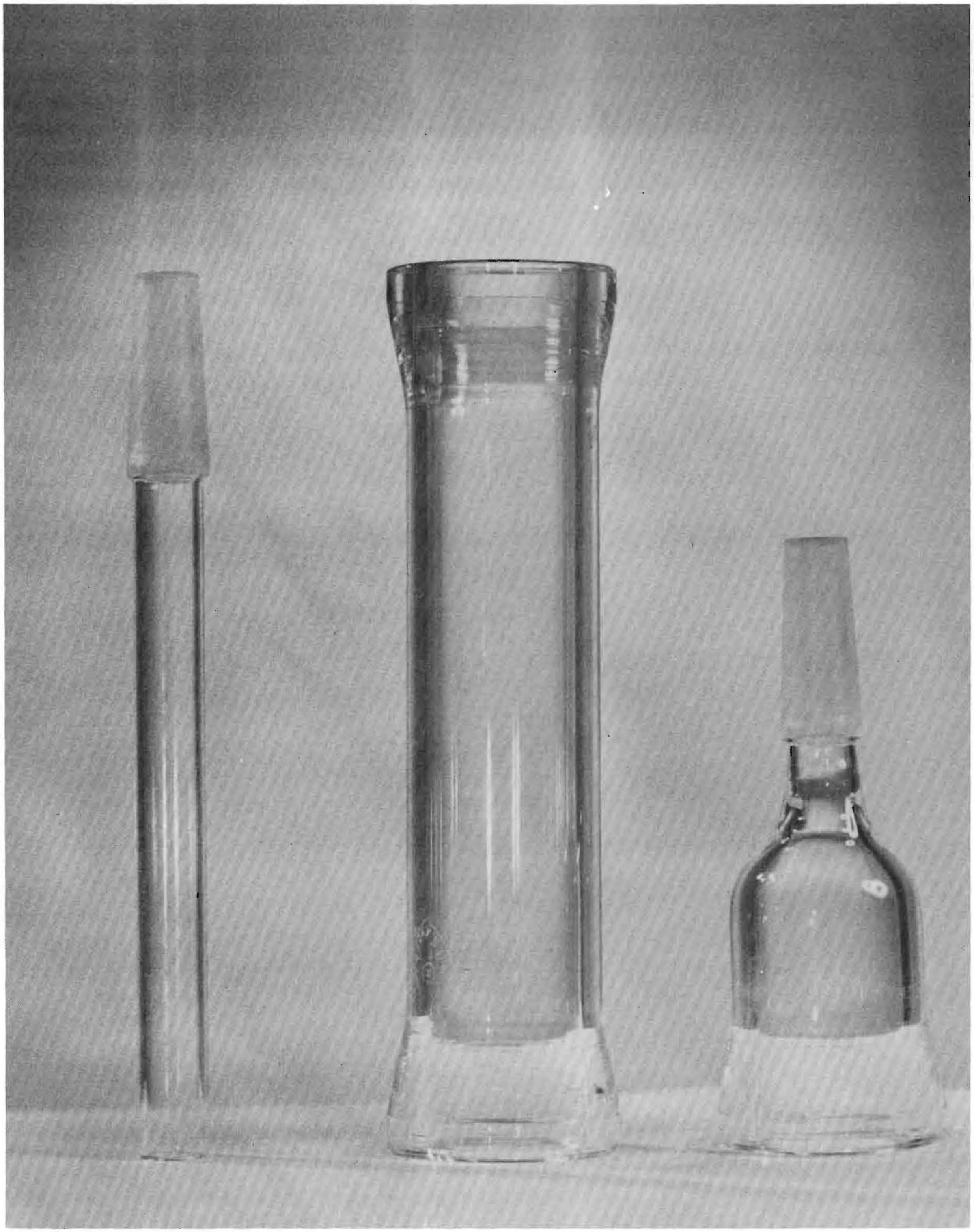

Figure 3. Basic Components of Construction for Upper Portion of Extraction Chamber.

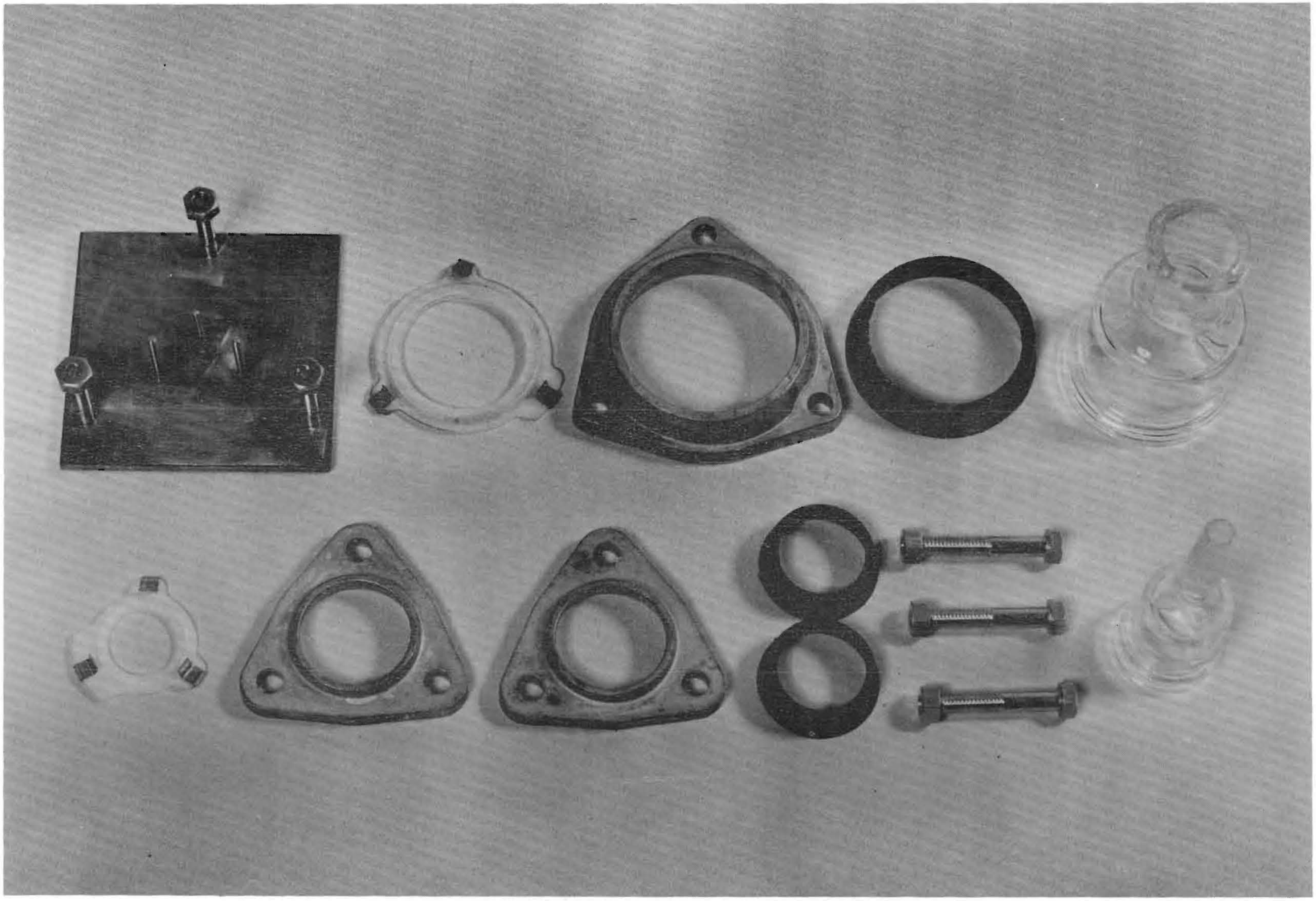

Figure 4. All Components of Extraction Chamber.

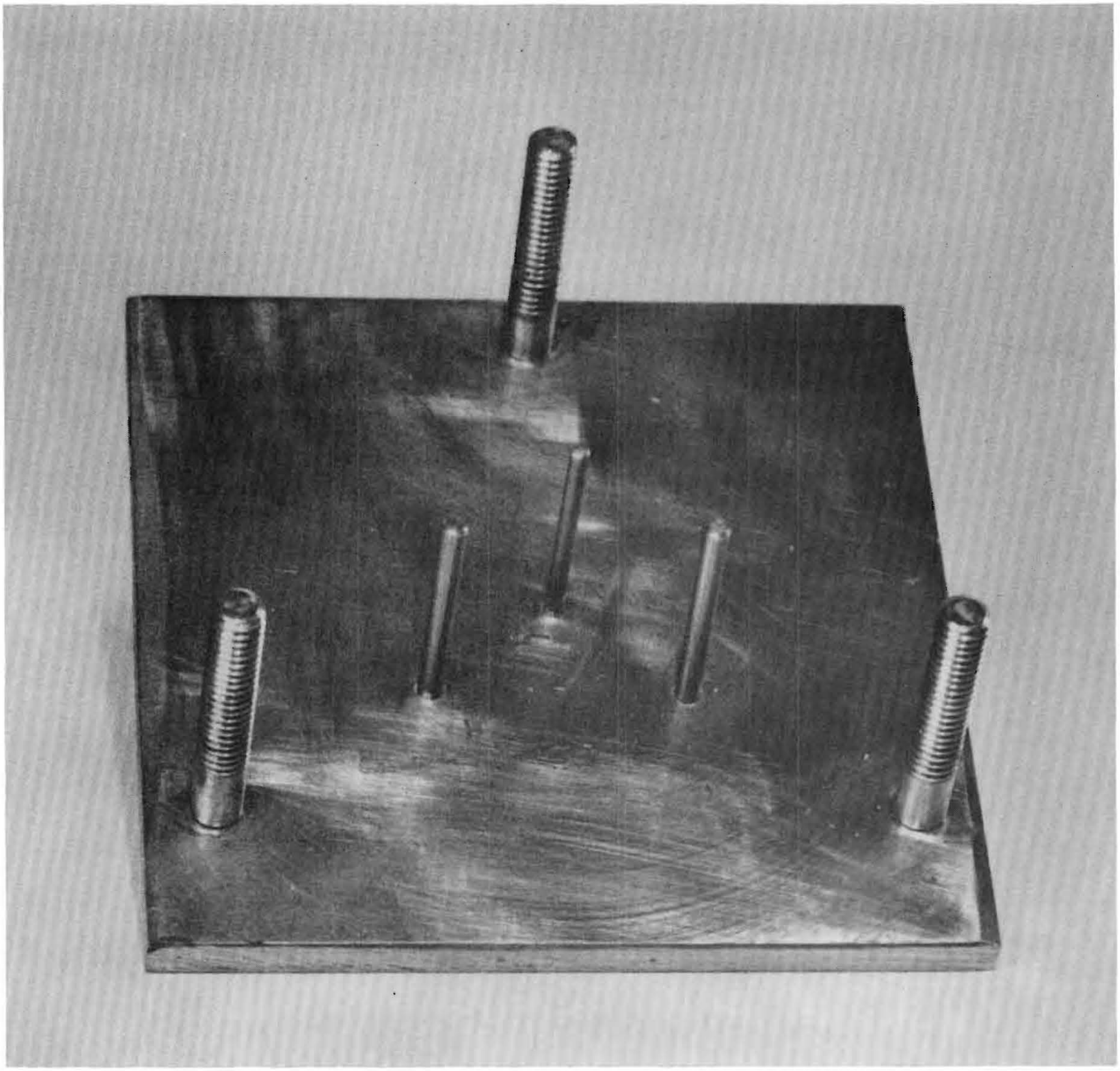

Figure 5. Base Plate.

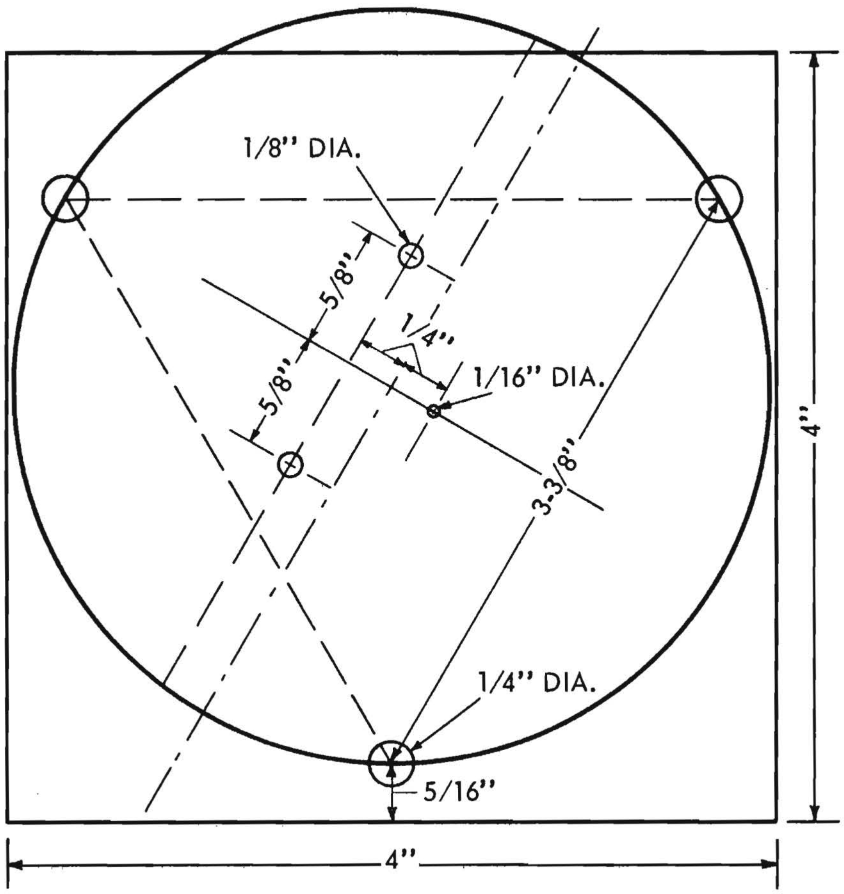

Figure 6. Construction of Base Plate for Gas Extraction Apparatus.

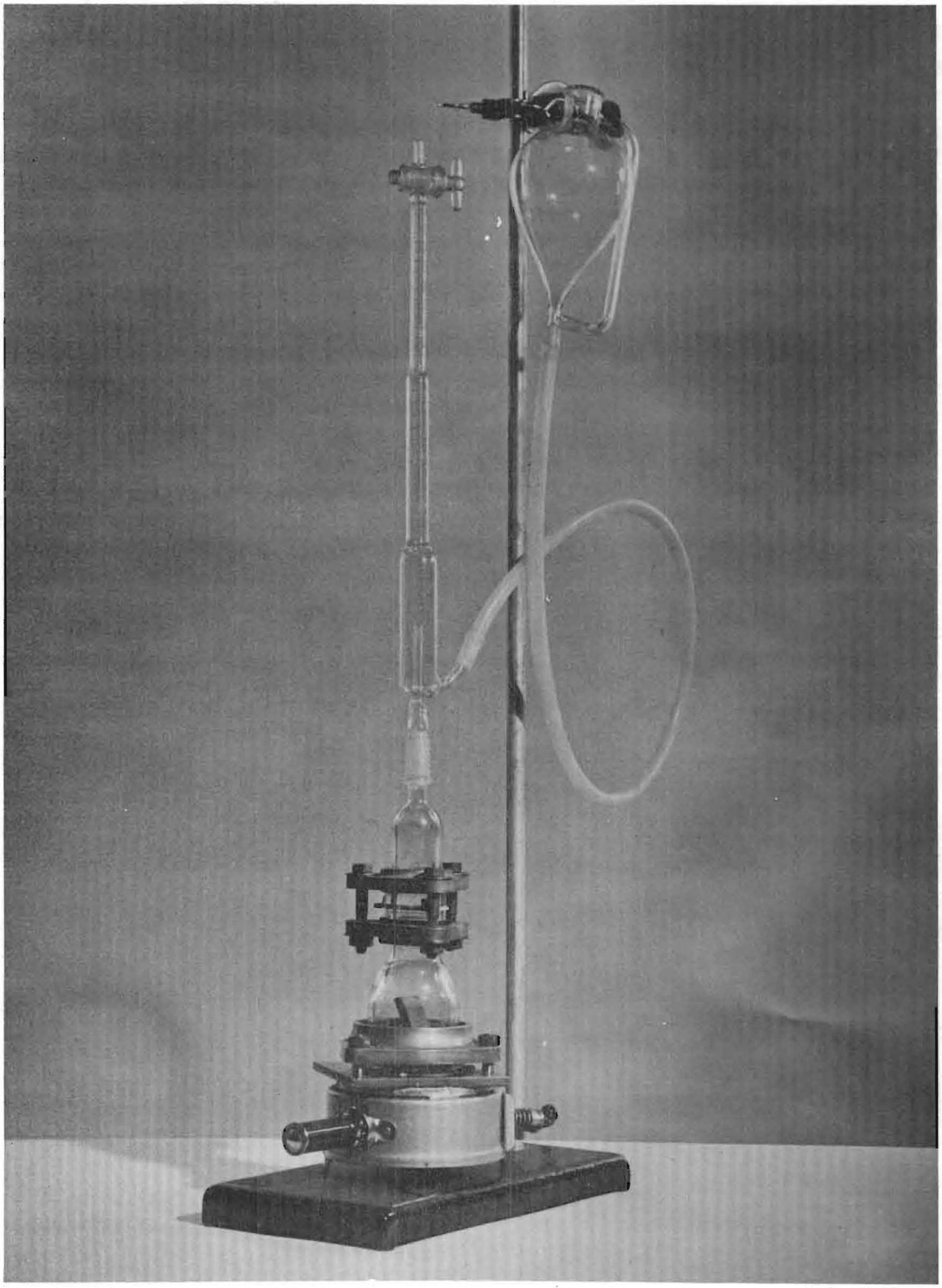

Figure 7. Assembly of All Parts of Extraction Apparatus.

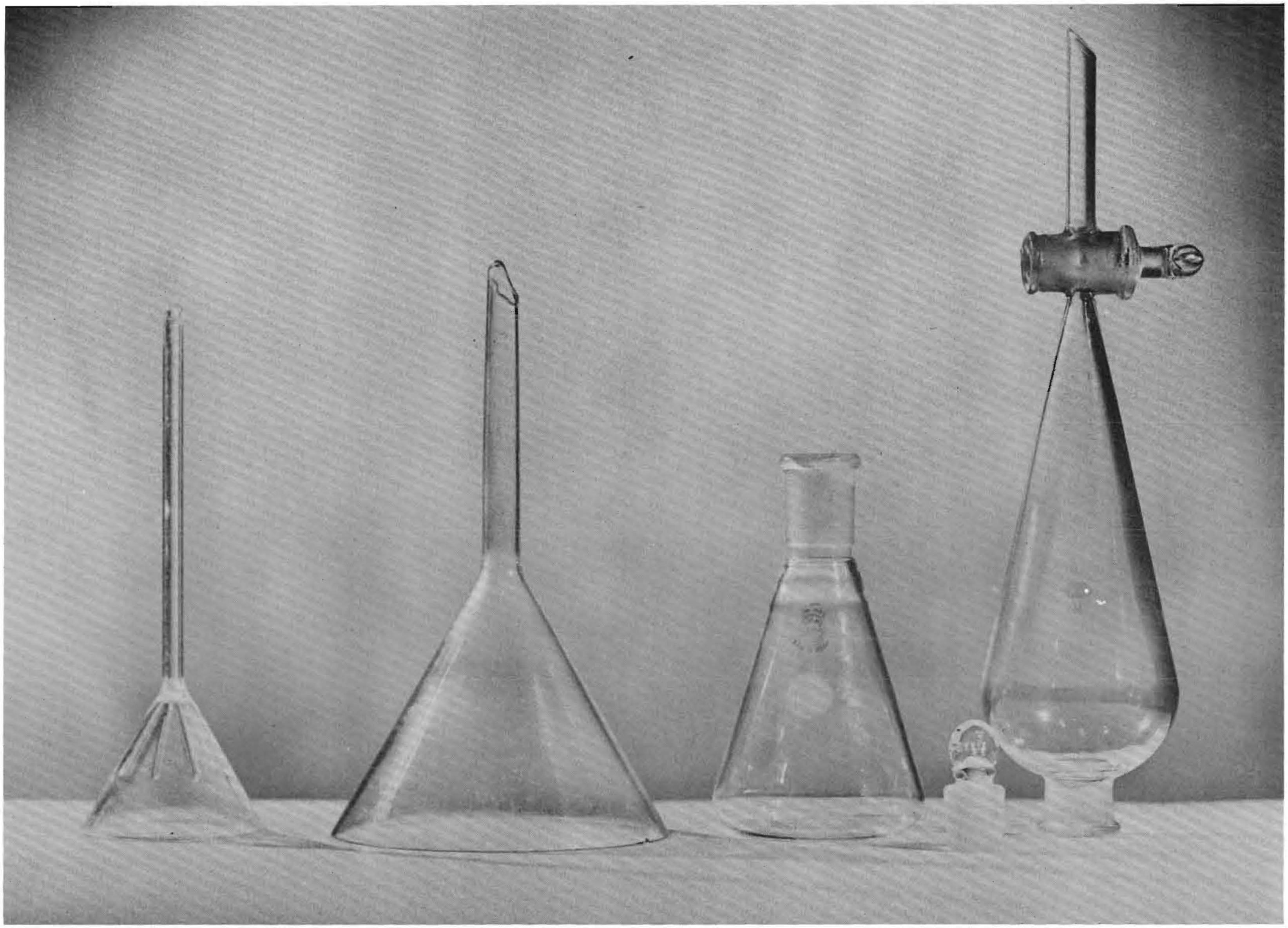

Figure 8. Accessory Equipment.